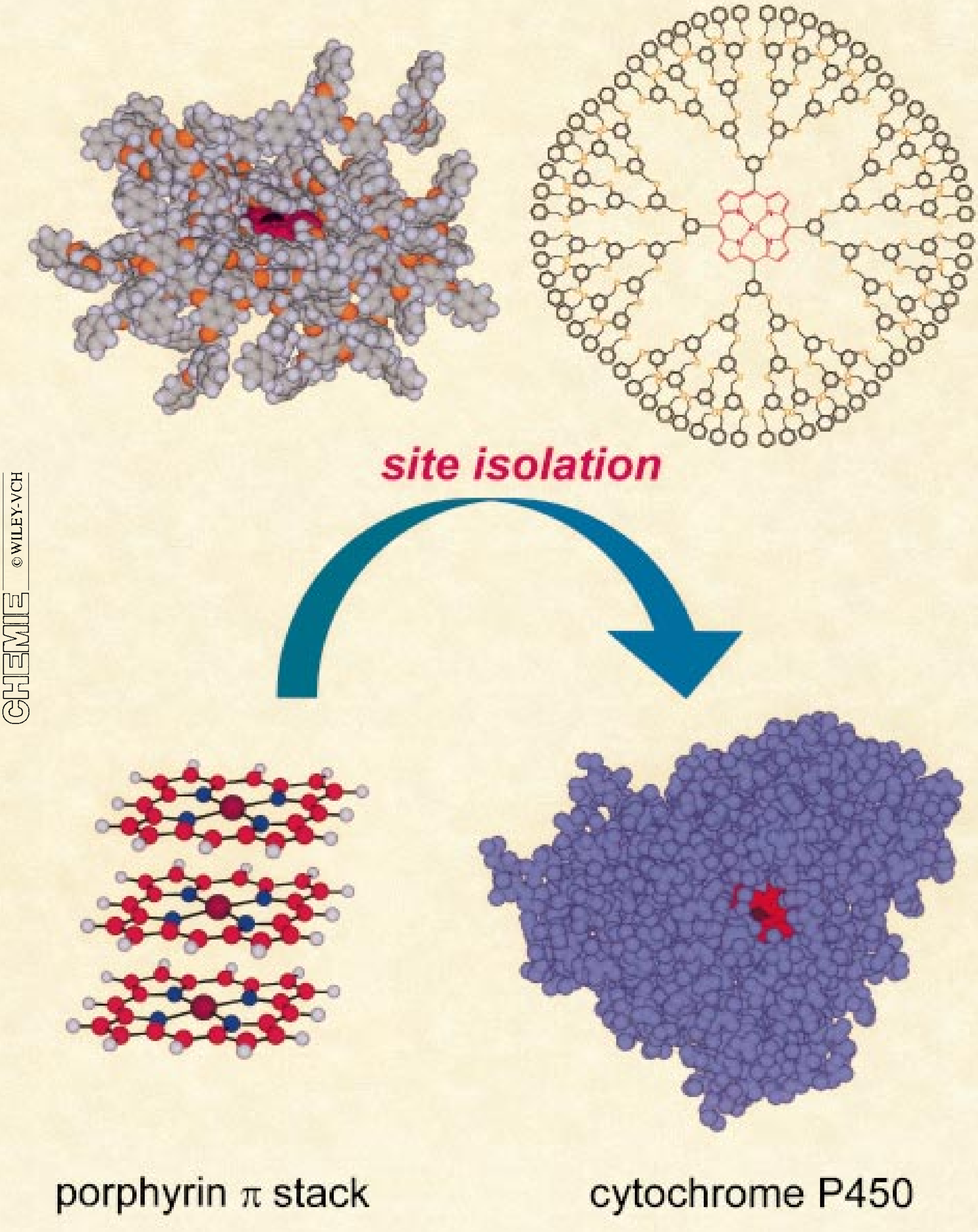
Dendritic Encapsulation of Function



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Dendritic Encapsulation of Function: Applying Nature's Site Isolation Principle from Biomimetics to Materials Science

Stefan Hecht and Jean M. J. Fréchet*

The convergence of our understanding of structure–property relationships for selected biological macromolecules and our increased ability to prepare large synthetic macromolecules with a structural precision that approaches that of proteins have spawned a new area of research where chemistry and materials science join with biology. While evolution has enabled nature to perfect processes involving energy transfer or catalysis by incorporating functions such as self-replication and repair, synthetic macromolecules still depend on our synthetic skills and abilities to mesh structure and function in our designs. Clearly, we can take advantage of our understanding of natural systems to mimic the structural features that lead to optimized function. For example, numerous biological systems make use of the concept of site isolation whereby an active center or catalytic site is encapsulated, frequently within a protein, to afford properties that would not be encountered in the bulk state. The ability of the dendritic shell to encapsulate functional core moieties and to create specific site-isolated nanoenvironments, and thereby affect molecular properties, has been explored. By utilizing the distinct properties of the dendrimer architecture active sites that have either photophysical, photochemical, electrochemical, or catalytic functions have been placed at the core. Applying the general concept of site isolation to problems in materials research is likely to prove extremely fruitful in the long term, with short-term applications in areas such as the construction of improved optoelectronic devices. This review focuses on the evolution of a natural design principle that contributes to bridging the gap between biology and materials science. The recent progress in the synthesis of dendrimer-encapsulated molecules and their study by a variety of techniques is discussed. These investigations have implications that range from the preliminary design of artificial enzymes, catalysts, or light-harvesting systems to the construction of insulated molecular wires, light-emitting diodes, and fiber optics.

Keywords: dendrimers · materials science · molecular devices · structure–property relationships

1. Introduction

The field of dendrimer chemistry[1] has undergone a very rapid development and has evolved from the discovery and the establishment of synthetic approaches to the characterization of dendrimer properties and the design of functional dendrimers.[2] The dendritic scaffold may therefore be used for the spatial arrangement of functionalities and the tailoring of properties through the interplay of the structural subunits. Dendrimers truly represent unique artificial building blocks as a result of the fine control that can be exerted over both their size and their molecular architecture, and therefore their three-dimensional nanoscale structure.[3]

Significant progress has been made in the use of dendritic frameworks to surround active core molecules. This process involves exploiting the inherent topological features of a dendrimer in which a core is surrounded by a branched shell that carries external "surface" groups. Dendritic shielding actually amounts to an encapsulation that can create a distinct microenvironment around the core moiety and hence affect its properties. This effect may result from the synergistic combination of the intrinsic chemistry of the building blocks of the dendrimer and the reduced accessibility of its core.

The encapsulation motif draws its inspiration from our increasing understanding of molecular biology. Enzymes provide an impressive demonstration of the profound effect a protein shell has on the active site of the enzyme. For example, the remarkable C–H bond activation performed by the heme protein cytochrome P450[4] and the long-range electron-transfer processes mediated by other cytochromes[5] would not be possible with unprotected hemes.[6] In many cases nature appears to create functional diversity by chang-

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ing the architecture around the active entity rather than by direct chemical modification of that entity. For instance, in a light-harvesting antenna complex of photosynthetic bacteria the bacteriochlorophyll molecules exist as two distinct chromophore subunits that have different absorption characteristics as a consequence of their spatial arrangement.[7] Working mostly with small molecules, chemists traditionally synthesize new molecules[8] to tailor the properties.[9] However, the challenge of mimicking nature by applying the design principle of property variation by architectural modification continues to fascinate.

In this attempt to summarize recent investigations dealing with dendritically encapsulated functionalities, we mainly focus on dendrimers with covalently attached cores that are either photochemically, electrochemically, or catalytically active. Clearly, today's accomplishments with dendrimer encapsulation pale in comparison to those achievable by natural systems, yet tantalizing leads have been uncovered.

2. Design Concepts, Synthetic Approaches, and Experimental Methods

The astonishing structural diversity of natural systems such as enzymes is achieved by a combination of different amino acid building blocks and a variety of interactions that lead to macroscopic organization. Seemingly complex folding processes give rise to the secondary and tertiary structure. Further interactions between the individual subunits can lead to even higher order quaternary structures, which are impressively demonstrated in "molecular machines" such as ATP synthetase. The globular structure of proteins is primarily based on the hydrophobic effect that exposes hydrophilic residues to the surrounding medium while sequestering hydrophobic fragments in the interior. The occurrence of specific interactions such as hydrogen bonding at the active site contributes to the stabilization of the transition states, and thereby favors certain reaction pathways. Without the benefit of evolution, dendrimers already provide unadorned steric protection and a unique—though still unsophisticated—"inner" environment that reflects the nature of its building blocks.

The geometric encapsulation of a core moiety by dendritic wedges ideally gives rise to a sphere or ovoid with a radius determined by the size of the core, as well as by the size and number of dendrons surrounding it. An alternative, if less common topology, wraps an inner elongated core or rigid rod with dendrons to afford cylindrically shaped dendrimers[10] (Figure 1). It is important to note that in all cases the steric crowding between the dendritic segments induces the shape of the molecule. The steric crowding itself is strongly dependent on the flexibility of the dendritic building block, the branching pattern, the size (or generation number) of the dendrons, as well as the interactions of the dendrons and the chain ends,

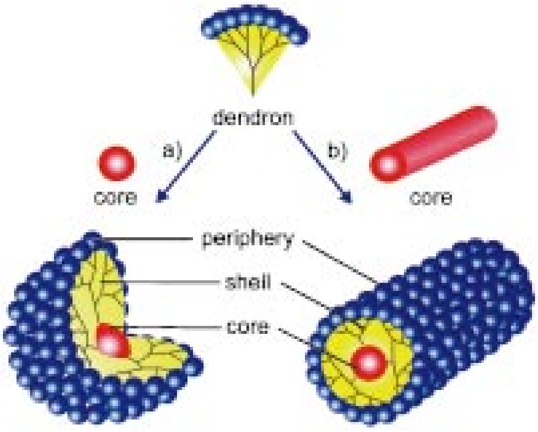

Figure 1. Attachment of multiple dendrons to polyfunctional cores gives rise to either spherically (a) or cylindrically shaped dendrimers (b). Idealized fully extended conformations are shown, in which the terminal groups (blue) are not mixed with the inner building blocks (yellow) or the core (red).

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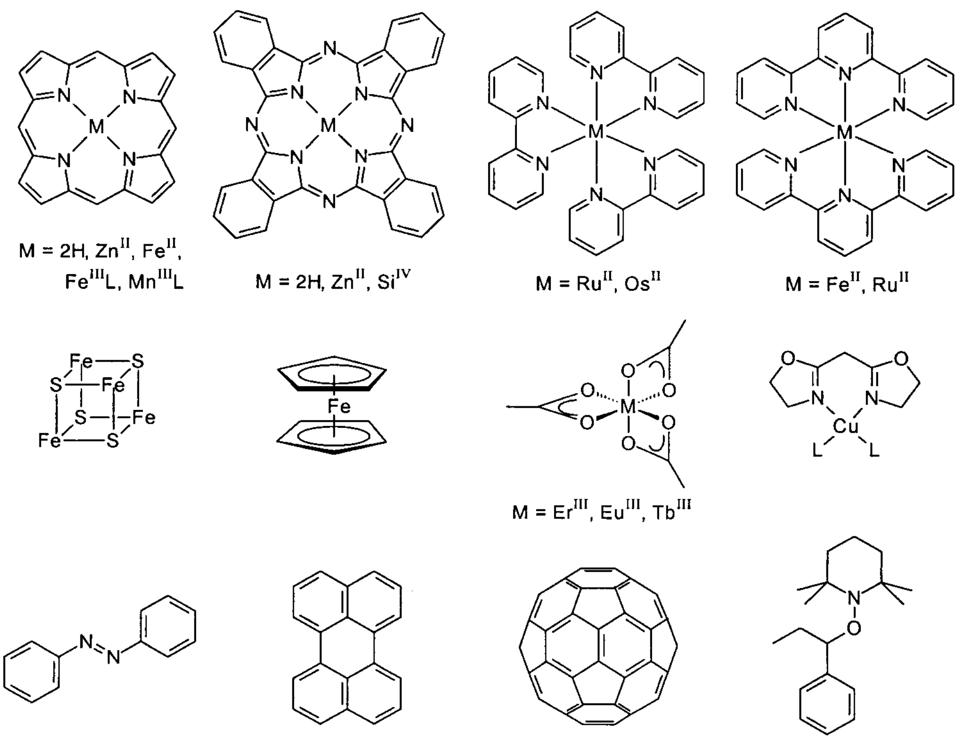
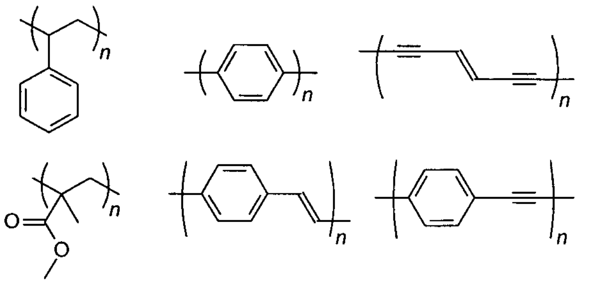
not only with each other but also with the surrounding medium. In addition, the degree of encapsulation of the core is a function of its size and the specific directional orientation of the dendrons.

Some of the most common core functionalities are shown in Schemes 1 and 2. For spherical dendrimers, these vary greatly in size—from compact metal ion complexes to large buckyballs or even porphyrins. In the case of cylindrical dendrimers, the most successful core motif to date involves rigid conjugated polymeric backbones, although even flexible backbones can give rise to cylindrical structures in the solid state.



Scheme 1. Examples of core functionalities exploited in spherical encapsulation.

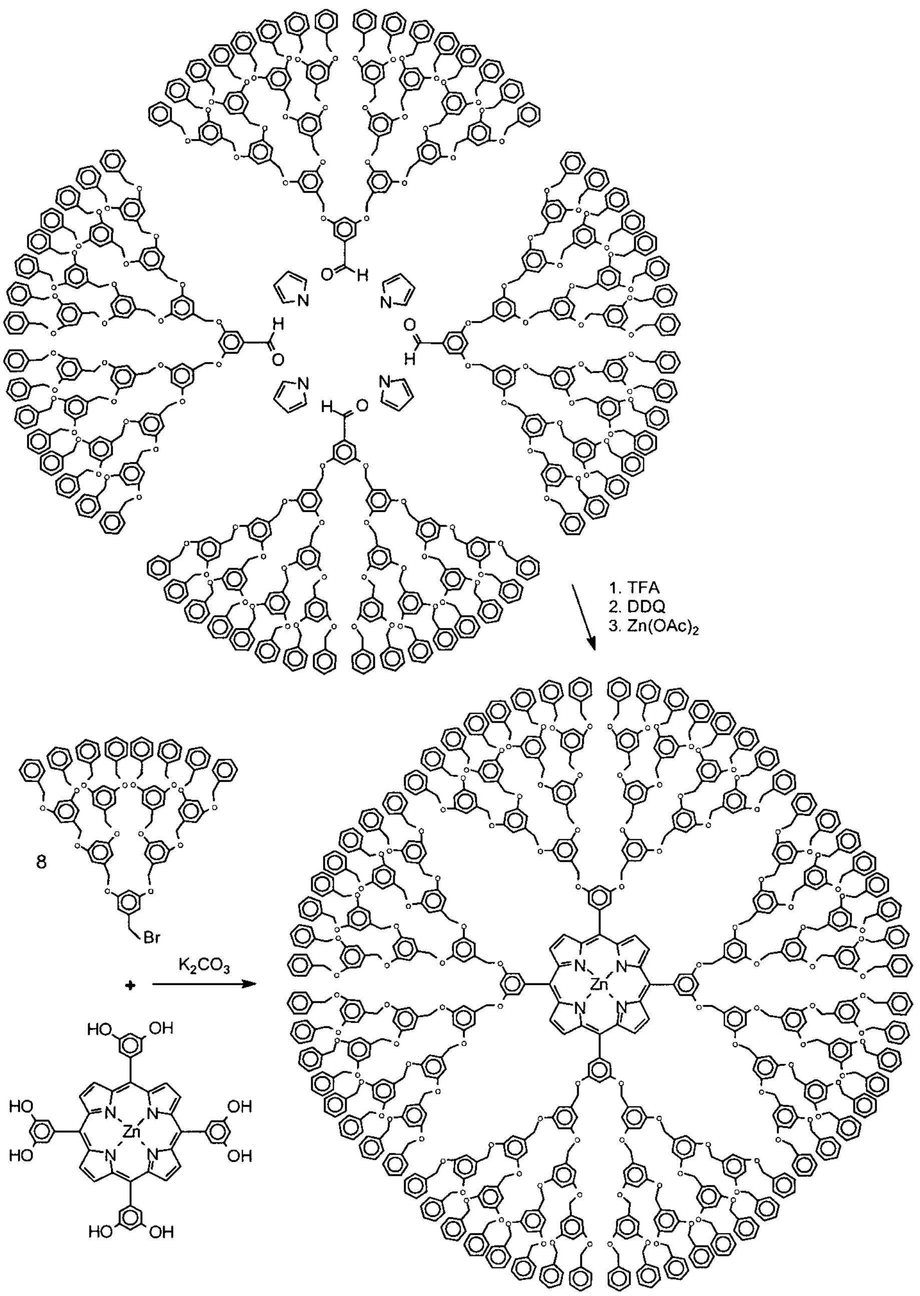


Scheme 2. Examples of core functionalities used in cylindrical encapsulation.

While both convergent and divergent strategies[1] may be used to achieve encapsulation, the convergent strategy appears to be more versatile as it avoids multiple synthetic operations on the often-exotic core and leads to more precise and uniform material.[2b] Within the last few years elegant synthetic protocols have been developed that form the core moiety directly from dendritic precursors in the final step of the sequence.[11] This direct method usually facilitates chromatographic purification, as a result of the more pronounced difference in the elution behavior of substrates versus products, whereas the more conventional process of grafting dendrons onto a polyfunctional core benefits from higher yields and added synthetic flexibility. For example, dendrimers with porphyrin cores have been prepared by Fréchet and co-workers and the chemical modification of a preformed core compared with a direct core-forming condensation (Scheme 3).[12] The reaction of zinc tetrakis(3,5-dihydroxyphenyl)porphyrin with poly(benzyl ether) dendrons under standard Williamson ether conditions gave the desired dendrimers. However, as the size of the dendrons increased, a larger excess was needed to drive the reaction to completion since the separation of partially reacted side products from the desired product was not possible. Despite this drawback, this modular approach is clearly advantageous since both the dendrons and functionalized porphyrin core are readily available. Alternatively, a Lindsey-type condensation[13] of dendritic aldehydes with an equivalent amount of pyrrole followed by metalation yielded the same products. The ease of the chromatographic purification associated with this approach is somewhat offset by the relatively low chemical yield of the Lindsey synthesis and is further affected by the high steric demand of this particular reaction.

An analogous study by Schlüter and co-workers explored the preparation of "cylindrical" moieties by the direct synthesis and core modification approaches (Scheme 4).[14] Poly(*p*-phenylene) was functionalized with a three- to fivefold excess of Fréchet-type dendrons using standard Williamson ether chemistry. Not unexpectedly, the use of higher generation dendrimers resulted in less than quantitative coupling reactions. In contrast, the use of dendrons with a focal point capable of acting as a monomer in a Suzuki-type polymerization led to the desired products even at higher generations. As a consequence of the inherent perfect dendritic coverage this direct approach is superior to the dendron-grafting route and it has since been further improved.[15] Numerous reviews with information regarding dendrimer synthesis and purification issues are available.[1]

In addition to the often complicated and time-consuming preparation and isolation of the compounds, the choice of experimental technique used to ascertain the effect of the dendritic shell is crucial and depends mainly on the core functionality. A variety of experimental tools have been employed to study the shape of the molecule in solution and to quantify the shielding of the core moiety (Table 1).

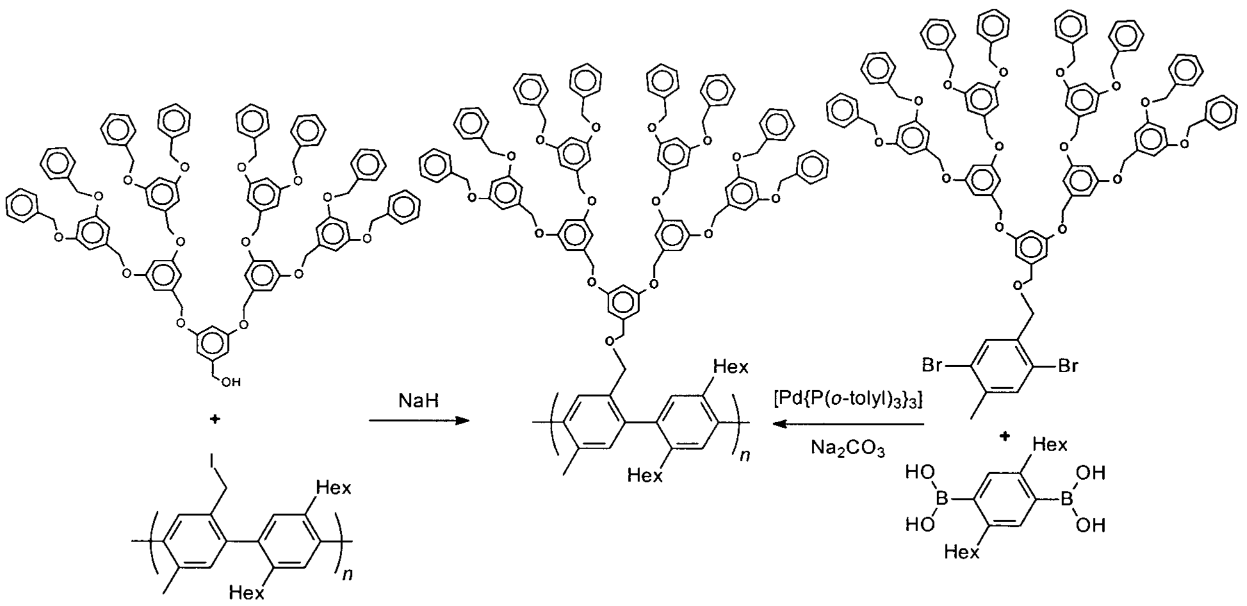


Scheme 3. Synthesis of a fourth generation dendrimer with a zinc porphyrin core using either chemical modification or direct condensation.[12] TFA = trifluoroacetic acid; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Changes in the microenvironment of core dyes are conveniently analyzed by absorption and emission techniques that rely on the stabilizing or destabilizing effect of the local medium on the electronic states of the chromophore. Parameters such as medium polarity (from spectral shifts)[16] or viscosity (from fluorescence anisotropy decays)[17] can be deduced from such measurements. Classic Stern–Volmer experiments have also been used extensively. Herein, the bimolecular deactivation of the excited state caused by penetration of an external quencher molecule through the dendritic shell allows for an evaluation of the accessibility of the core.[18] Other kinetic methods that do not involve a fluorescence signal include cyclic voltammetry (CV)[19] as well as chemical reactions performed within the dendrimer itself. The occurrence of reversible or irreversible electron transfer and the change in redox potential in CV measurements provide information about the isolation of the core moiety; whereas, rates, chemical yields, and selectivity in kinetic studies give insight into substrate diffusion and the binding to the reactive or catalytic site. A vast number of physical methods are available to complement the above mentioned techniques, for instance, NMR relaxation experiments can be used in connection with paramagnetic cores,[20] with conventional proton relaxation,[21] or even to probe the entire dendritic framework.[11] Other methods dealing with dendrimer conformation and dynamics, such as gel-permeation chromatography (GPC), differential viscometry, and computational methods have been reviewed recently by Bosman, Janssen, and Meijer.[1b]

3. Photoresponsive Systems

The environment of a chromophore is able to affect its photophysical properties, such as absorption and emission characteristics, as well as its photochemical behavior. We have already mentioned nature's perfection in creating such environments and even to spatially arrange multiple chromophores with respect to each other to further enhance performance in a synergistic fashion. In a first simple approach to study the effect of the microenvironment on the properties of an encapsulated dye, Hawker, Wooley, and Fréchet attached solvatochromic probes to the core or focal point of dendrimers.[16a] Analysis of the UV/Vis absorption spectra of a series of Fréchet-type dendrons with a *p*-nitroaniline solvatochromic probe attached to their focal point (Figure 2) showed a pronounced bathochromic shift of the absorption maxima in nonpolar solvents such as CCl_4 or toluene with increasing generation. The most dramatic change occurred between the third and fourth generations, presumably as a consequence of the transition from an extended to a more globular structure that better encapsulates the core. Correlation with Taft's solvent polarizability parameter π^*[22] indicated that at high generation the local environment near the chromophore resembles that of highly polar solvents such as DMF.



Scheme 4. Synthesis of a third generation dendrimer with a poly(*p*-phenylene) core using either chemical modification or a dendritic monomer route.[14]

Table 1. Experimental techniques available for the evaluation of the microenvironment and accessibility of the core moiety.

Technique	Information used for the evaluation of the dendritic shielding effect	Ref.
UV/Vis and emission spectroscopy	spectral shift and intensity	[16, 21, 25, 29, 30b, 31, 58–60]
time-resolved emission spectroscopy/ fluorescence anisotropy	excited-state lifetime from signal decay/anisotropy decay	[17, 21c, 25, 34b]
emission quenching	bimolecular quenching rate constant from Stern–Volmer analysis	[18, 23–26, 27b, 30a, 30c, 85]
cyclic voltammetry	occurrence and ease of electron transfer to an electrode surface/shift in redox potential	[24, 39, 40, 42, 43, 45–47, 58]
kinetics	rate constants and selectivities of a given chemical reaction	[21a, 21b, 30d, 32, 65–68, 71–79, 86]
NMR	spin lattice relaxation times	[11, 20, 21]

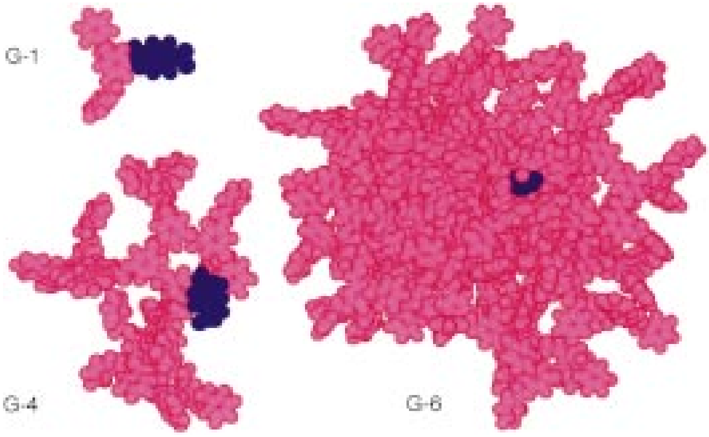


Figure 2. Dendritic *p*-nitroanilines as solvatochromic probes. The space-filling model illustrates increasing encapsulation of the focal chromophore (blue) by the dendrimer backbone (pink).[16a]

In subsequent work, Moore and co-workers utilized the emission of phenylacetylene dendrimers modified with an electron donor at the focal point to probe the local environment.[16b] An anomalous spectral shift in the fluorescence maximum of the charge transfer state was observed with higher generations. An abrupt change was observed between the fourth and fifth generations, which suggests the occurrence of dendritic encapsulation and corroborates the earlier findings of Hawker et al.[16a] Even more recently, Smith and Müller studied Newkome-type dendrimers having a tryptophan core, and correlated the observed spectral shifts to the ability of the solvent to form hydrogen bonds and therefore stabilize the emitting state.[16c]

Dendrimers with a porphyrin core have been of considerable interest for their potential in catalysis as well as artificial photosynthesis, and have been studied extensively in the Aida, Diederich, and Fréchet laboratories. In their initial publication,[23] Aida and co-workers observed that the fluorescence of a fourth generation dendrimer was quenched more efficiently than that of a smaller first generation dendrimer by a small molecule quencher such as Vitamin K_3. However, the opposite effect was observed when a larger molecule such as a first generation dendritic porphyrin in the form of a free base was used as the quencher. These results led to the conclusion that, in higher generation dendrimers, the dendrons act as a trap for small molecules for which they have an affinity, but cooperatively serve as a barrier for larger ones. Later, investigations performed by Fréchet and co-workers[24] using a similar series of dendrimers and benzyl viologen as the quencher showed a comparable increase in quenching efficiency at higher generation. Sadamoto et al. introduced peripheral anionic groups that led to pre-complexation of the cationic methyl viologen quencher and were able to observe an electron-transfer reaction through the dendrimer backbone.[25] Consequently, efficient fluorescence quenching in self-assembled ensembles of free base porphyrins and zinc porphyrins having oppositely charged peripheral groups was reported.[26] In an alternative and very elegant approach to demonstrate the accessibility of the core as well as the influence of the size of the penetrating molecule, Aida and co-workers examined the interaction of dendritic imidazoles with dendrimers containing a zinc porphyrin core (Figure 3).[21a] Evaluation of the measured binding constants showed that dendritic interpenetration is greatly diminished at higher generations of both the zinc porphyrin and the ligand.

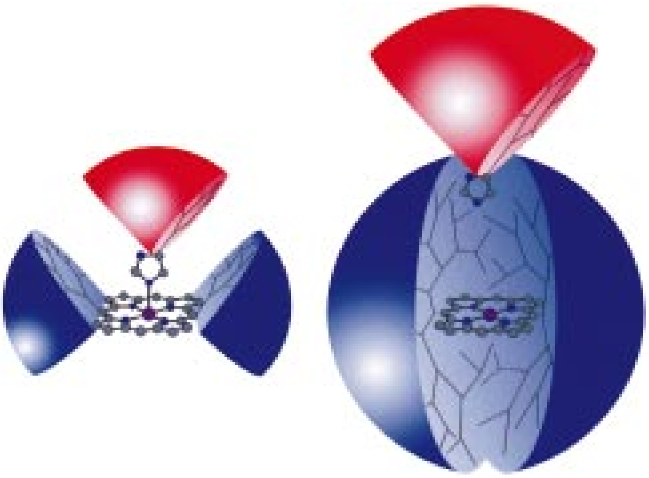
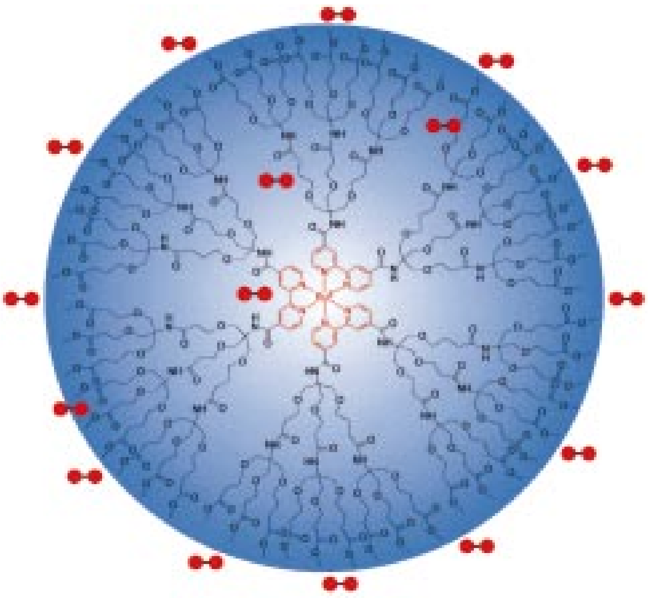


Figure 3. Ligation of dendrimers with zinc porphyrin cores (blue) by dendritic imidazoles (red). The interaction of a low generation complex and ligand gives rise to a high binding constant (left), whereas the interaction of a high generation complex and ligand leads to a small binding constant (right).[21a]

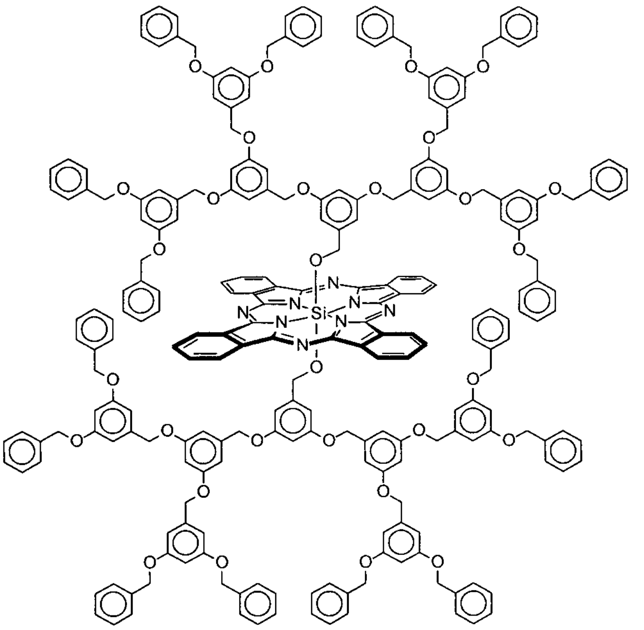


Scheme 5. An increase in the emission quantum yield and excited state lifetime in dendrimers with a tris(bipyridine)ruthenium core is attributed to diminished quenching by molecular oxygen (red).[27a]

Further insight into the role of the dendritic shell as a barrier for external quenching agents, leading to an increasing lifetime of the excited state, was provided by the groups of Balzani and Vögtle, who investigated dendrimers with a tris(bipyridine)ruthenium core.[27, 28] In aerated solution, the higher generation Newkome-type poly(ether amide) dendrimers (Scheme 5) exhibited increased emission quantum yields as well as enhanced excited-state lifetimes as a result of the shielding effect of the dendritic shell limiting the quenching by molecular oxygen.[27a] The reduced quenching efficiency of molecular oxygen can be attributed to its lower solubility in the dendritic interior, a possibly decreased diffusion rate, and/or better core solvation. More recently, the authors found a similar trend with related poly(benzyl ether) dendrimers.[27b] These studies enable a comparison of the effect of the different dendrimer backbones, namely the Newkome- and Fréchet-types. A solution of the second generation Newkome-type compound in aerated acetonitrile at room temperature has an excited state with twice the lifetime and an emission that is red-shifted by 30 nm relative to the third generation Fréchet-type compound. Clearly, the more polar poly(ether amide) dendrons stabilize the metal→ligand charge transfer (MLCT) excited state more efficiently than the less polar poly(benzyl ether) dendrons.

One of the major aims of the introduction of bulky dendrons around a central moiety has been to prevent self-aggregation of dye molecules in the solid state. This self-aggregation is mainly caused by π-π stacking interactions. The isolation of the individual chromophores greatly enhances their optical properties as a result of reduced self-quenching. Unfortunately, as the size of the core dye increases, larger or higher generation dendrons have to be used to achieve efficient shielding.[17b] To overcome this problem, McKeown and co-workers took advantage of the coordination sphere of a silicon phthalocyanine to attach Fréchet-type dendrons in the axial positions.[29a, 30] The third generation compounds having an axial dendritic substitution (Scheme 6) showed a significant decrease in exciton coupling in the solid state as a consequence of an efficient separation of the chromophores, while the equatorial analogues exhibited strong aggregation.

Kawa and Fréchet demonstrated recently the use of self-assembled dendritic carboxylate ligands to encapsulate lanthanide ions, thereby greatly improving their luminescence properties.[31] Assembly of three anionic dendrons around erbium(III), europium(III), or terbium(III) ions (Figure 4) led to an enhancement of luminescence efficiency with increasing generation as a result of site isolation of the lumophores, which drastically reduced their rate of self-quenching. In the context of fiber optics applications, the match of the 980 nm excitation with the typically used pumping wavelength makes the dendrimers with the erbium(III) cores, as well as their conceptual analogues, interesting candidates for glass-fiber amplifiers. In addition, the authors observed an antenna effect which resulted in the efficient sensitization of the core luminescence by the dendritic ligands. Interestingly, the energy transfer was dramatically reduced in an isomeric complex having a 1,2,5-branching pattern instead of the more



Scheme 6. Dendritic substituents in the axial position of silicon phthalocyanine moieties prevent self-aggregation by π-π stacking interactions in the solid state.[29]

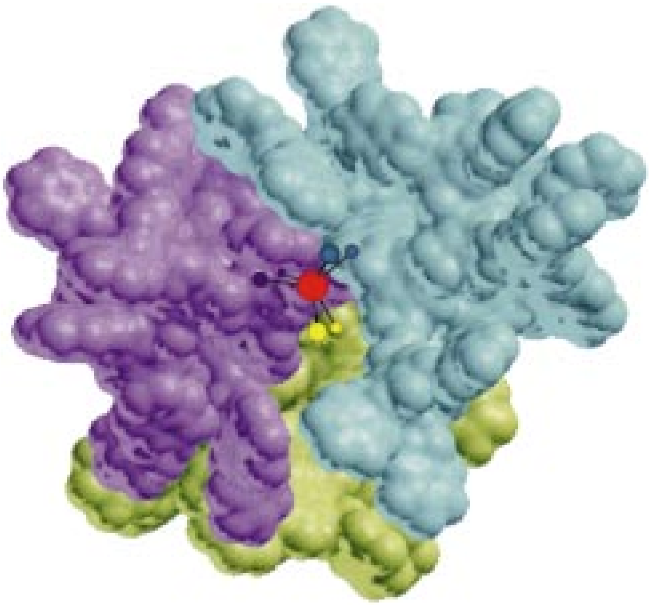


Figure 4. The assembly of three dendritic wedges (light blue, violet, and yellow) having a focal carboxylate functionality around a lanthanide ion (red) leads to site isolation and greatly enhanced luminescence properties.[31] The core has been moved to the front for better visibility.

common 1,3,5-substitution at the focal point. Clearly, the focal aromatic structure plays a crucial role in the observed antenna effect.

Recently, Jiang and Aida thoroughly studied similar morphology effects on the antenna effect in a series of free base porphyrins substituted with various numbers of high-generation dendrons (Figure 5).[21c] Migration of excitation energy was found to be extremely efficient in the fully labeled porphyrins, which indicated complete encapsulation and cooperativity of the dendritic subunits in the spherical morphology.

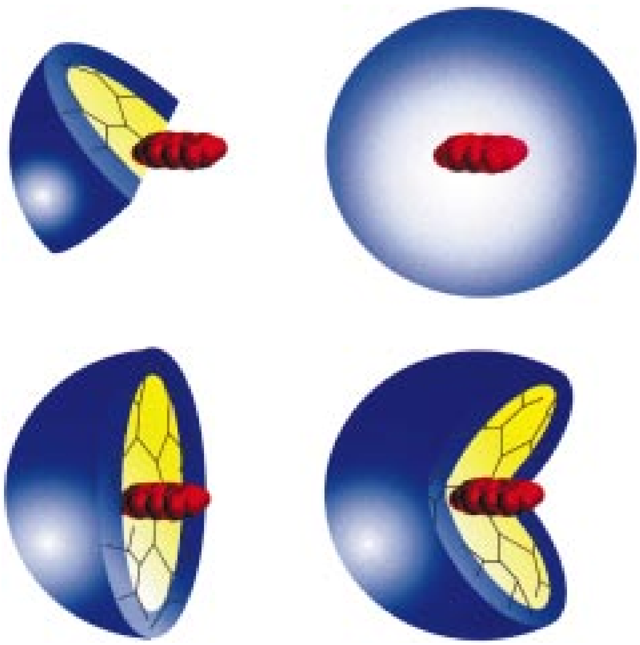
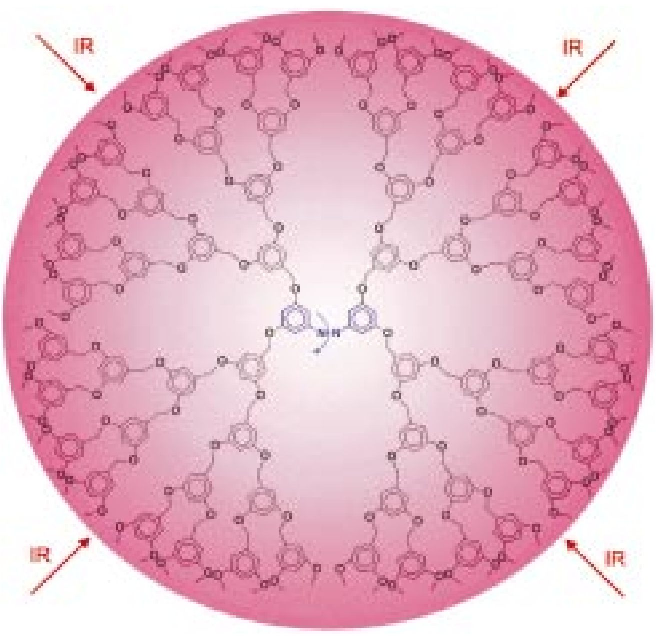


Figure 5. Increasing the number of dendritic substituents leads to more efficient encapsulation of the porphyrin core (red). Energy transfer from the dendrimer backbone to the core is greatly enhanced in the spherical morphology.[21c]

An impressive demonstration of the effect of morphology on energy transfer was provided by the same authors investigating the IR-accelerated *cis*–*trans* isomerization of an azobenzene core moiety (Scheme 7).[21b] They noted that after achieving full encapsulation by using either fourth or fifth generation dendrimers the rate of isomerization was two orders of magnitude faster under controlled IR irradiation than was the case for a purely thermal reaction. This phenomenon was reported to occur only when a particular



Scheme 7. The harvesting of multiple IR photons by a fifth generation dendrimer with an azobenzene core leads to an acceleration of the *cis*–*trans* isomerization.[21b]

IR stretching frequency of the aromatic branching units (1597 cm^{-1}) was employed for irradiation. The authors concluded from the activation barrier for the *cis – trans* isomerization (21.4 kcal mol^{-1}) that this process involved approximately five low-energy IR photons (1597 cm^{-1} corresponds to 4.6 kcal mol^{-1}). Junge and McGrath investigated the effect of large dendrons on the rate of thermal *cis – trans* reversion of photo-isomerizable units using somewhat similar molecules.[32, 33] Not unexpectedly, given the large degree of conformational freedom that prevailed in the investigated poly(benzyl ether)-type dendrimers, the small disturbance created by isomerization at the core is quickly dissipated through the bulky but flexible shell.

In addition to steric protection, a dendrimer molecule is uniquely suited to arrange multiple peripheral functional groups around a single core unit. By introducing an energy-transfer interaction or similar electronic "communication" between the periphery and the core, the design of dendritic light-harvesting antennae becomes feasible. In such systems an array of terminal donor chromophores may collect many photons and transfer their energy to the core acceptor unit, which can also be excited independently of the periphery. Since emission is observed from the core only, the system serves as a spatial and spectral energy concentrator or "molecular lens" (Figure 6). Essentially, this mimics the primary events in photosynthesis, where the light-harvesting complex funnels its excitation energy to the special pair leading to subsequent charge separation. Two types of systems which either use the dendritic architecture solely as a scaffold[34] or involve the dendrimer backbone in the energy-transfer event[21b,c, 30c, 31, 35] have been explored. Our group has recently shown that an amplification of the core acceptor emission can be achieved in high-generation dendrons labeled with multiple donor chromophores at the periphery.[34a–c] The amplification effect has its origin in the enhanced donor absorption cross-section and the extremely fast rate of through-space energy transfer to the core, which gives rise to efficient light harvesting.[34b] Another key finding was reported by Moore and co-workers, who demonstrated a significant acceleration of energy transfer within dendrimers having an internal energy gradient, which arose from a stepwise decrease in the HOMO – LUMO gaps of the branching units when progressing toward the acceptor.[35b] Balzani and co-workers constructed bipyridine-based polynuclear metal complexes and were able to control the direction of energy transfer through alteration of the excited-state energies by introducing appropriate metal ions.[35f] This strategy impressively demonstrates how supramolecular chemistry can be used to assemble multiple chromophores and furthermore control their relative orientation.

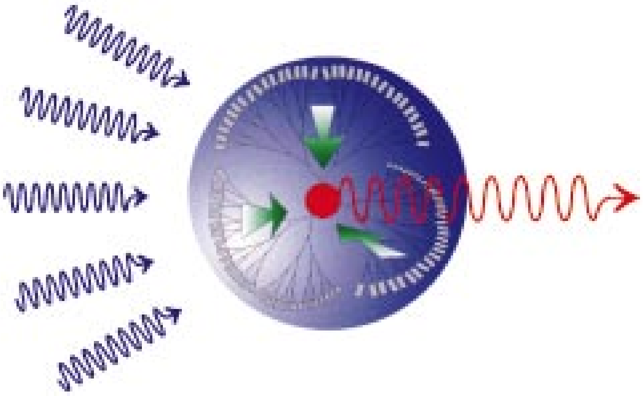
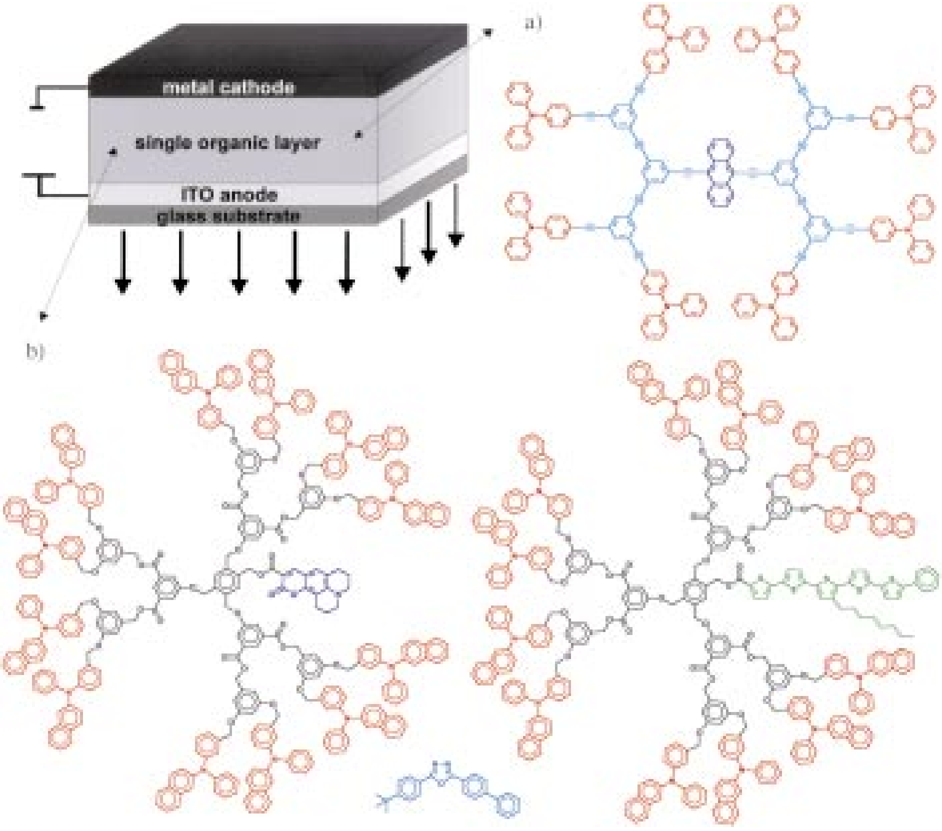


Figure 6. Illustration of a dendritic light-harvesting antenna. The absorption of light of a broad spectral range by peripheral chromophores leads to an enhanced emission from the core (red) as a result of efficient energy transfer (green arrows).

From a more applied perspective, dendritic scaffolds have been used to spatially arrange the different components necessary for the construction of organic light-emitting diodes. The good film properties obtained from spin casting combined with the formation of a single layer only (having either one or multiple components) offer the potential advantage for the very economic fabrication of devices (Scheme 8). Moore and co-workers have described devices



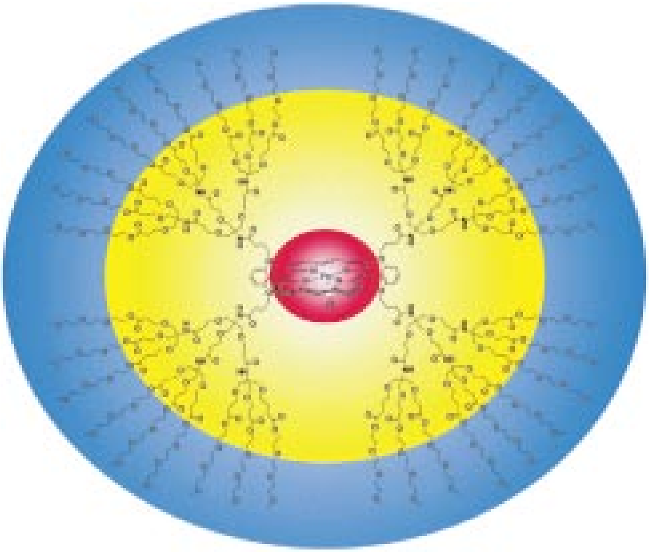
Scheme 8. Single layer organic light-emitting diodes consisting of one component (a)[36] or multiple components (b) for color tunability.[38] Hole-transporting units are shown in red, electron-transporting units in cyan, and the lumophores in their respective emission color.

based on phenylacetylene dendrimers having a luminescent anthracene core and peripheral tertiary aromatic amines.[36] The triaryl amines in their dendrimers served as the hole-transporting element, while the phenylacetylene dendrons acted as electron transporters. The dendrimer backbone was shown to be capable of efficient energy transfer,[35a,b] and charge recombination within the dendrimer led to a directed transduction of excitation energy to the emitting core. Although a good correlation was found between the photoluminescence and the electroluminescence spectra, the devices had a very low efficiency as a result of self-quenching caused by solid-state aggregation.

The device efficiency of a related system based on stilbene dendrimers[37] was found to increase by nearly an order of magnitude from the first to the second generation, again demonstrating the value of the site-isolation concept. More recently, Freeman et al. prepared naphthyldiphenylamine-terminated poly(benzyl ether) dendrimers having coumarin or pentathiophene cores (Scheme 8b).[38] Two-component single-layer devices consisting of the dendrimer, which served as both hole transporter and emitter, as well as an oxadiazole derivative, which acted as the external electron transporter, were fabricated and good matching of the photoluminescence and electroluminescence was observed. The modular design of this approach and the partial site isolation of the central dye by the dendritic framework allows for a combination of dendrimers having differently emitting cores and thus affords a color-tunable system.

4. Electroactive Systems

For decades biologists and chemists have been fascinated by electron transfer proteins and their superior design that allows for efficient charge transfer over long distances. Cytochrome c and ferrodoxin, for instance, participate in the respiratory chain by delivering the necessary electrons to the reaction center that reduces oxygen to water. Dendritically encapsulated metalloporphyrins and their electrochemistry have been studied extensively as simple synthetic models for heme-containing electron-transfer proteins such as cytochrome c. Diederich and co-workers systematically changed the microenvironment of the core by varying the generation number to gain further insight into the role of the protein shell in achieving remarkably high oxidation potentials in such enzymes.[39] Initially, the authors reported that the increasingly electron-rich environment around the core in higher generation Newkome-type dendrimers with zinc porphyrin cores led to facilitated oxidation and inhibited reduction processes.[39a,c] Subsequently, the first water-soluble dendritic iron porphyrins were synthesized.[39b,c] Remarkably, the second generation dendrimer dissolved in water (Scheme 9) exhibited a Fe^{III}/Fe^{II} reduction potential 420 mV more positive than that of the first generation compound. This finding was attributed to the enhanced shielding of the iron porphyrin core which led to reduced contact with the external solvent and therefore destabilization of the higher charge oxidation state. In more recent work, Diederich and co-workers reported the preparation of related dendrimers with iron porphyrin cores that had two tethered imidazole ligands to provide intramolecular axial ligation.[39d] Again, the reduction took place at a much more positive potential when sufficient dendritic shielding was achieved.

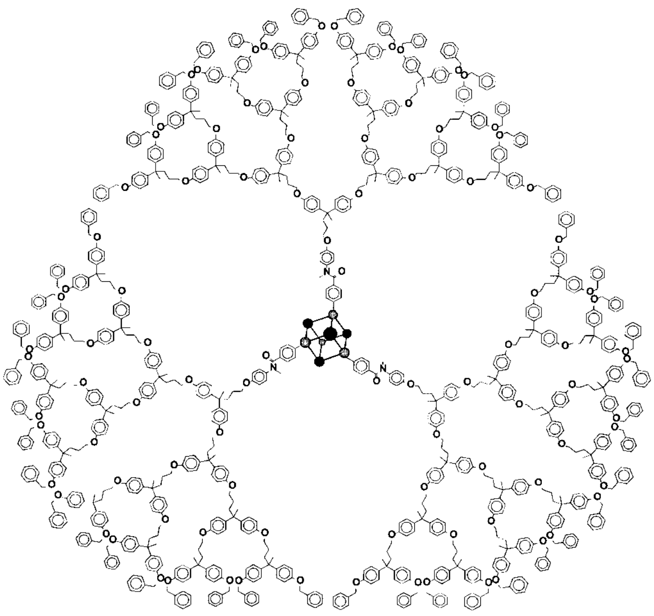


Scheme 9. A unimolecular dendrimer with an iron porphyrin core as a dendritic cytochrome c mimic.[39] The hydrophobic interior (yellow) encircling the redox center (red) is itself surrounded by a hydrophilic periphery (blue).

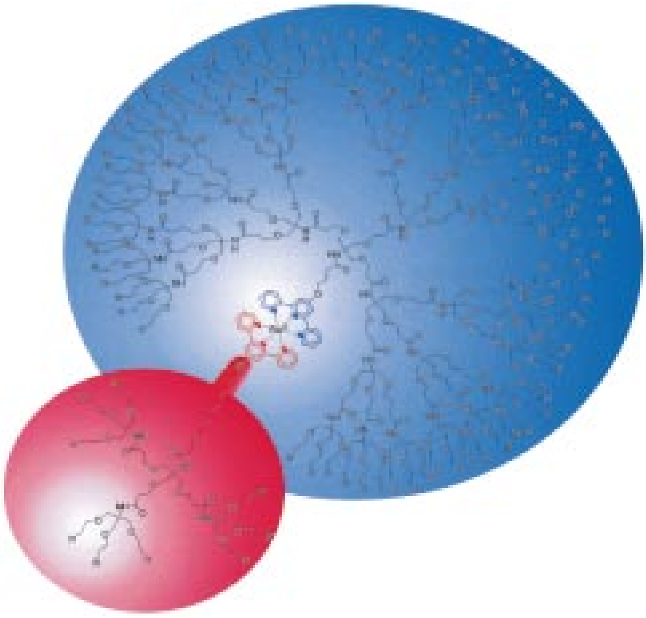
A related study by our own research group involving poly(benzyl ether) dendrimers with zinc porphyrin cores (Scheme 3)[24] demonstrates most clearly the effect of the dendritic environment on the electrochemical characteristics of the core. Increasingly slow electron transfer kinetics were observed, as judged by a decrease in the peak current and an increase in the peak potential differences, as the size of the dendritic shell increased. In fact, shielding was so effective for the fourth generation compound that no electron transfer at all could take place. This result illustrates clearly the dendritic shell effect that leads to a more hindered approach of the core to the electrode. Both studies[24, 39] independently illustrate that changes in redox potential with increasing core isolation can mainly be correlated to dendritic solvation, namely, the difference between the chemical nature of the dendritic interior and the exterior solvent.

In an attempt to mimic a non-heme iron-based electron-transfer protein, such as ferrodoxin Gorman and co-workers studied cubic iron–sulfur clusters (Scheme 10)[40] prepared through a ligand-exchange reaction using poly(aryl ether) dendrons having an aromatic thiol functionality at their focal point.[41] The increasing steric bulk of the higher generation ligands led to a more difficult reduction of the core, both kinetically and thermodynamically—as indicated by shifts of reduction potentials to more negative values and increasing peak potential differences. As illustrated above, electron transfer between the core and the electrode slows down in higher generations as a consequence of dendritic insulation.

Newkome et al. also took advantage of electrochemical methods (CV) to probe the interaction of "lock" and "key" dendritic segments mediated by a bis(terpyridine)ruthenium(II) complex.[42] Whereas a combination of second genera-



Scheme 10. Dendrimers with iron–sulfur cluster cores as dendritic ferrodoxin mimics.[40]

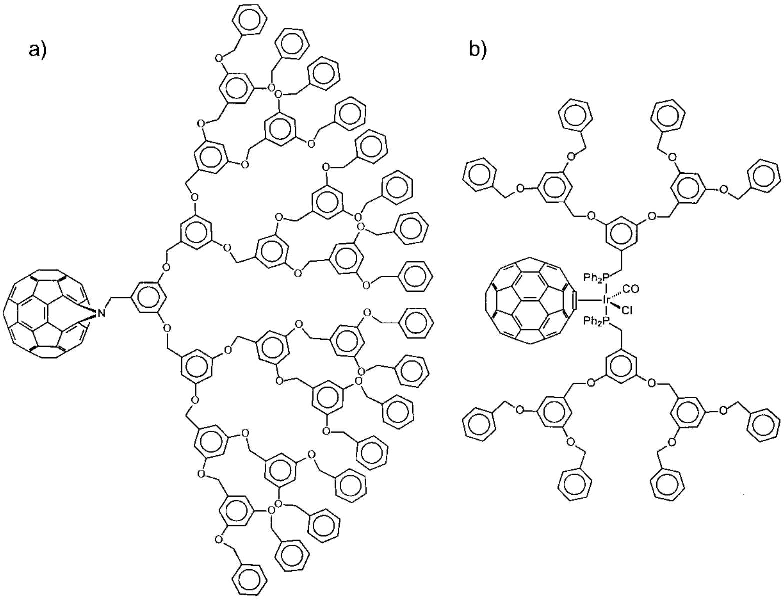


Scheme 11. The interaction of a second generation "key" (red) with a fourth generation "lock" segment (blue) leads to an efficient shielding of the core.[42]

tion "key" and second generation "lock" displayed a reversible redox cycle, the use of the fourth generation "lock" (Scheme 11) led to a completely irreversible behavior, which indicated highly efficient shielding of the ruthenium(II) core. Chow and co-workers subsequently reported a systematic study[43] of related bis(terpyridine)iron(II) complexes encapsulated within poly(ether) dendrimers.[44] X-ray photoelectron spectroscopy showed no significant changes in the bonding environment of the central iron atom in different generations. Once again, CV revealed an increasingly difficult metal redox process in higher generation dendrimers as a result of the thicker dendritic coating leading to an increased remoteness of the metal center from the electrode surface.

A detailed analysis of the observed electrochemical irreversibility was provided by Kaifer and co-workers, who thoroughly studied ferrocene modified with dendritic ligands.[45] The authors showed that the heterogeneous electron-transfer rate constant as well as the diffusion coefficients decreased as the generation number increased.[45a, 46] Strong orientational effects on the heterogeneous electron transfer were also observed when ionizable surface groups capable of interacting with a modified electrode surface were introduced on the dendrimer.[45b]

The chemistry of fullerenes has seen many creative forays in the past two decades and it continues to stimulate a broad spectrum of research activity. While C_{60} itself is significantly smaller than most dendrimers, combinations involving the two globular species with their extremely versatile chemistries and tunable properties appeared attractive. Hence, the first C_{60}-dendrimer hybrids were reported by the groups of Wudl and Fréchet, who used a conventional Williamson ether synthesis of fullerenes carrying two phenolic sites with Fréchet-type dendrons having benzylic bromides at the focal point.[47a] This initial approach was complicated by side reactions related to the functionalized fullerene and required preparative gel-permeation chromatography (GPC) for purification. An alternative synthesis involving the coupling of dendritic azides to C_{60} proved better, and the hybrid (Scheme 12 a) displayed a dramatically enhanced solubility relative to fullerene itself.[47b] CV measurements indicated that the attached dendron had an insulating effect on the fullerene. In a very elegant study Catalano and Parodi demonstrated the reversible binding of a Vaska-type iridium complex containing dendritic phosphane ligands coordinated to C_{60} (Scheme 12b).[48] More recently, Hirsch and co-workers attached twelve Fréchet-type den-



Scheme 12. Dendritic fullerenes having either a covalent (a)[47] or a coordinative linkage (b).[48]

drons to a fullerene by a cyclopropanation route.[49] Subsequently, they also introduced a tetraphenylporphyrin unit and observed photoinduced electron transfer in their dendritic donor–acceptor dyad.[50]

In addition to the numerous examples of organic dendrimer shells used to encapsulate various electroactive cores presented above, metallodendrimers based on coordinative linkages involving multifunctional ligands and connecting metals have recently received much attention.[3c,d, 51]

5. Cylindrical Encapsulation and Electroactive Systems

The dimensionality of a cylinder (Figure 1) introduces the directionality required for charge-transfer processes. Therefore, dendritically substituted conjugated rigid rods[52, 53] should ideally give rise to an insulated “molecular wire”, an attractive goal for molecular-scale electronics.[54] Schlüter and Percec have independently proposed cylindrical dendrimers based on steric repulsions between dendritic segments attached to a central linear polymeric core to enforce an overall extended, rodlike shape (Figure 7).[10] Following up on early work on polymers with dendritic pendant groups by Hawker and Fréchet,[55] Schlüter and co-workers carried out a definitive study of “dendronized” polymers.[14, 15, 56] Their efficient and elegant synthetic approaches afforded well-defined macromolecules consisting of poly(styrene) or poly(*p*-phenylene) cores substituted by Fréchet-type polyether dendrons. Small-angle neutron scattering experiments showed that both the dendron generation and the presence of charged peripheral groups had a strong influence on the diameter of the cylinderlike molecule.[56d] In another study, scanning force microscopy revealed that the poly(*p*-phenylene) core nanorods (Figure 7) were approximately 90 nm long and 4.8 nm in diameter.[15]

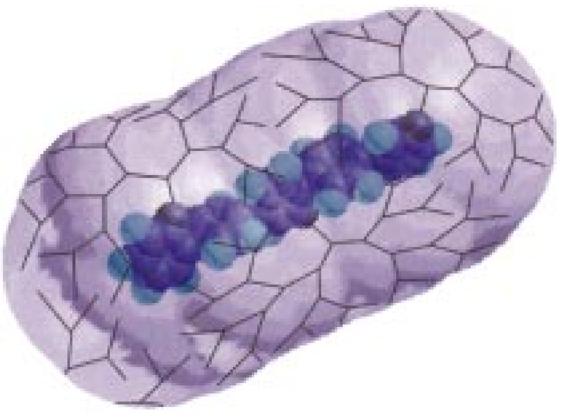


Figure 7. Illustration of a cylindrically shaped dendrimer formed as a consequence of the steric repulsion between dendritic substituents attached to a rigid rodlike core, for example, poly(*p*-phenylene).

In an exquisite and completely different approach Percec et al. reported on styrenic and methacrylic polymers with tapered dendritic side chains that form cylindrical structures in the solid state through a supramolecular self-assembly process reminiscent of that of the tobacco mosaic virus (Figure 8).[57] It was shown that polymerization of dendritic monomers within the dendritic coat was accelerated[57b] and that the degree of polymerization of the resulting polymer determined the overall shape of the macromolecule, namely, cylindrical or spherical, as a consequence of maximized self-encapsulation.[57c]

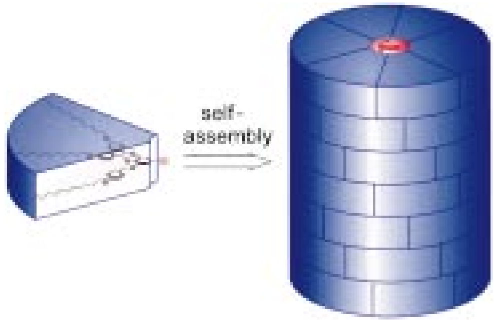


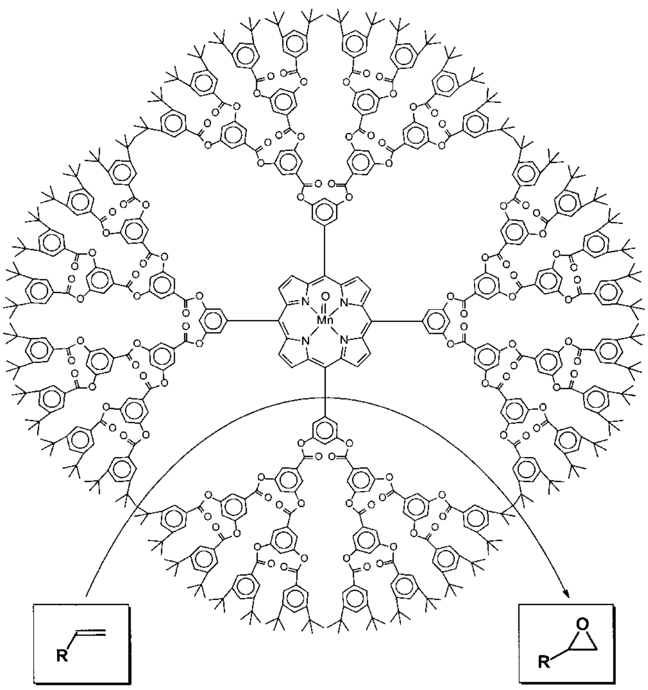
Figure 8. Self-assembly of linear polystyrene (red) having tapered dendritic side chains (blue) into cylindrical superstructures.[57]

Building on these concepts, many promising systems using conjugated rodlike cores have been reported recently. For instance, Diederich and co-workers described the synthesis and study of dendritic poly(triacetylene) oligomers of precise lengths.[58] CV experiments suggested that the dendritic layer protected the central backbone without altering its electronic properties, as shown by UV/Vis spectroscopy. An important advantage of the monodisperse oligomers over the related polymerized species is the precise control over the length of the molecular wire. Bao et al. investigated emissive dendrimers with poly(phenylenevinylene) cores and showed that the bulky dendritic wedges enhanced main-chain separation in the solid state as verified by X-ray diffraction measurements.[59] Therefore, self-quenching is reduced in the solid state—a necessary prerequisite for high photoluminescence and electroluminescence quantum yields. In a related study Sato et al. reported on dendrimers with poly(phenyleneethynylene) cores as blue light emitting dendritic rods.[60] The authors found that the quantum yields for luminescence approached unity for the fourth generation compound, even when used at high concentration in solution. The efficiency was further enhanced by a facile energy transfer from the dendrons to the core leading to efficient light harvesting. An amphiphilic cylinder has also been described very recently by Bo et al.[61] This type of structure opens the possibility of building higher order architectures similar to the natural ion channels based on an array of amphiphilic peptide helices. The surface differentiation was accomplished by the attachment of hydrophobic and hydrophilic dendritic segments to the monomer followed by polymerization.

6. Catalytically Active Systems

The size of a dendrimer is roughly comparable to that of many enzymes and, just like enzymes, dendrimers are able to create a microenvironment around a reactive site. While nature has had an ample opportunity to optimize enzymes through evolutionary processes, one of our best tools for the optimization of dendrimers is mimicry, even if based on grossly simplified models. Significant advances have been made in the last few years and more sophisticated dendritic molecules that perform more and more catalytic operations will continue to appear. Numerous reports have already outlined approaches to the use of dendrimers as molecular-scale chemical reactors. Ideally, the dendritic superstructure would provide a tool to tune and enhance the activity and selectivity of a single encapsulated active site.[62, 63]

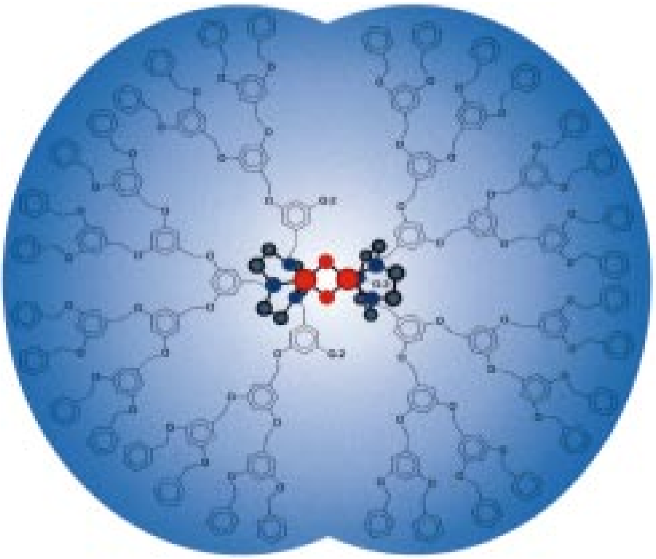
Among the most attractive targets is the mimicry of natural oxidation catalysts, in particular, heme-based oxygenases.[64] Manganese porphyrins carrying oxidatively robust poly(phenyl ester) dendrons were reported by Moore and co-workers[65] and were found to catalyze the shape-selective[66] epoxidation of alkenes when iodosobenzene was used as the oxidizing agent (Scheme 13). In both intra- and intermolecular competition studies, the second generation dendrimer-based catalyst was up to four times more selective towards less-hindered terminal double bonds than a simple manganese tetraphenylporphyrin used for comparison purposes. The dendritic catalysts showed excellent oxidative stability as a consequence of their efficient shielding. More recently, Kimura et al. published their first results of employing dendrimers with cobalt phthalocyanine cores to catalyze the oxidative transformation of thiols to disulfides using molecular oxygen as the oxidant.[30d] The authors found that the catalytic activity of the second generation catalyst dropped by 20% relative to that of the first generation, which suggested there was no significant restriction in the penetration of the substrate into the dendrimer. Not surprisingly, the larger, higher generation catalyst displayed enhanced stability as a result of its better protection by the dendritic shell.



Scheme 13. Shape-selective olefin epoxidation using dendrimers with a manganese(III) porphyrin core as catalysts.[65]

Heme proteins are known to bind dioxygen either prior to activation, to yield the catalytically active oxo species, or simply for transport reasons, such as in monomeric myoglobin or tetrameric hemoglobin. Dendritic iron(II) porphyrins have been investigated in an attempt to mimic oxygen binding. Jiang and Aida reported that the lifetime of the oxygen adduct dramatically increased with increasing dendritic shielding and leading to 95% survival after two months in the case of the somewhat stiffer fifth generation dendrimer.[67] The authors suggested that the more crowded dendritic poly(benzyl ether) barrier lowered the effective gas permeability and acted to reduce the entry of water molecules, therefore, providing both steric and hydrophobic protection to the oxygen complex. Collman, Diederich, and co-workers measured the oxygen and carbon monoxide equilibrium binding constants of their Newkome-type poly(ether amide) dendrimers using 1,2-dimethylimidazole as the axial ligand to form a five-coordinate, high-spin iron(II) precursor complex.[68] They found a remarkably high oxygen affinity, 1500 times greater than that of the T state of hemoglobin. This result was attributed to possible hydrogen-bonding interactions of the amide protons with the terminal oxygen atom. Interestingly, the measured carbon monoxide affinity was very low.

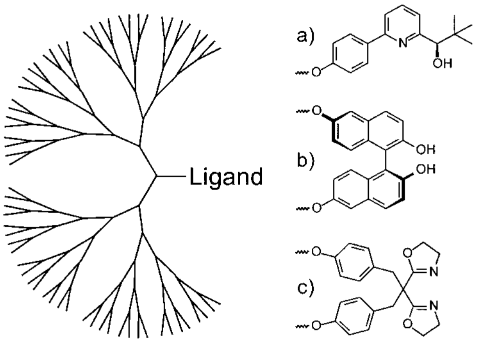
Multicopper motifs[69] have also been investigated as non-heme models for oxygen carriers.[70] Enomoto and Aida described the oxygen driven self-assembly of a copper-ligating dendrimer to yield a bis(μ-oxo)copper dimer (Scheme 14).[71] The decay of the oxygen complexes was very dependent on dendrimer size, with high generation dimers displaying longer lifetimes. Kinetic analysis revealed that a more negative entropy of activation was the cause for the slower unimolecular decay. However, the oxygen adduct cannot be formed at all at a higher generation because of the steric bulk of the dendritic subunits.



Scheme 14. Dendritic non-heme dioxygen carrier. A bis(μ-oxo)copper dimer based on a triazacyclononane (TACN) – copper(II) complex is shown.[71]

The application of dendrimers in the design of sensors for sulfur dioxide gas was demonstrated with poly(phenyl ester) dendrimers bearing multiple platinum pincer complexes.[72] These metalated dendritic sensors showed a direct optical response, were highly selective towards sulfur dioxide, and fully reversible, thus providing the opportunity to tune the detection sensitivity through variations in the number of platinum sites.

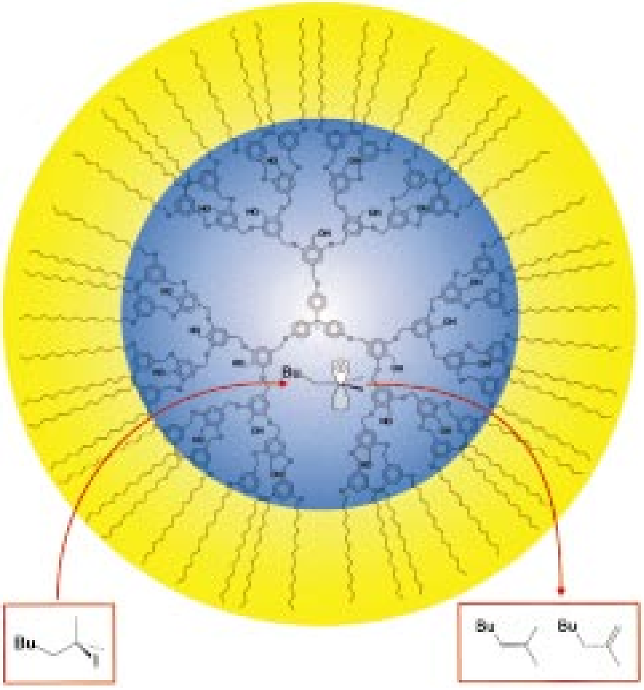
Brunner introduced dendritic ligands carrying optically active groups for enantioselective catalysis.[73] The molecules, termed "dendrizymes", were designed to transfer the chiral information inherent in the dendrimer backbone over a long range to the asymmetric metal center. However, enantioselectivities were usually found to be rather low. Interestingly, in one case a 1,3,5-branched ligand led to a rate acceleration whereas the 1,2,5-isomer showed a rate retardation. This finding is in agreement with other studies mentioned earlier,[21c, 31] which illustrate the important effect of the dendritic branching pattern on the ultimate properties of the material. Dendritically expanded chiral ligands have been explored in the asymmetric addition of carbonyl groups. Whereas Bolm and co-workers used dendritic pyridyl alcohols (Scheme 15a) for the asymmetric addition of diethylzinc to benzaldehyde,[74] Yoshida et al. reported on dendrimers with binaphthol core as chiral ligands in the titanium-mediated allylation of the same substrate (Scheme 15b).[75] The key result in both studies is that the enantioselectivities remained constant with increasing generation. A detailed mechanistic analysis has been performed by Chow and co-workers, who investigated dendritic bis(oxazoline)copper(II) catalysts in Diels–Alder reactions (Scheme 15c).[76] Precomplexation of the dienophile to the catalyst became increasingly difficult as the generation number increases. The rate of the subsequent reaction of the catalyst–substrate complex with the diene remained initially constant, then dropped when changing from the second to the third generation. For the higher generation catalyst, a slightly enhanced selectivity was observed for sterically less demanding dienophiles. A similar finding was reported by van Leeuwen and co-workers, who investigated palladium-catalyzed allylation reactions using a bisphosphane ligand incorporated in a carbosilane dendrimer.[77] Increasing the generation number of the catalysts led to a rate decrease as well as a change in the regioselectivity of the catalyst.



Scheme 15. Dendritically modified chiral ligands for asymmetric catalysis.[74–76]

It is clear that simply building chirality into the dendritic analogue of a small molecule catalyst is not sufficient to produce enzyme-like catalytic enhancements. In addition, increasing the generation number and therefore the thickness of the dendritic shell may—depending on the flexibility and exact nature of the building block—lead to increasingly difficult mass transport and therefore diminished catalytic activity. Clearly, the application of more thorough design concepts including tailored microenvironments and even structural features that assist in transport and in lowering the energy of key transition states and intermediates will be required before dendritic catalysts can reach their full potential.

In collaboration with Hawker, our research group has recently designed a very simple dendrimer catalyst (Scheme 16) that incorporates design features that favor a low-energy transition state while also providing for the preferential entry of the reagents and thermodynamically driven exclusion of the product to avoid product inhibition of the catalytic site.[78] The dendrimer behaves as an (inverse) unimolecular micelle-like container with a hydrophilic interior environment that stabilizes polar transition states and intermediates, and a hydrophobic exterior that helps to solubilize the catalyst and drive products away from the catalytic site. The catalyst was tested in simple E1-type eliminations from tertiary alkyl halides. As a result of their polarity, the alkyl halide moieties are drawn to the highly polar core, where formation of the carbocationic intermediate and subsequent elimination occurs to yield the nonpolar alkene that is then rapidly driven from the core to the



Scheme 16. A unimolecular reverse micelle that efficiently catalyzes the elimination of tertiary halides.[78] The nonpolar corona (yellow) shields the polar interior (blue) of hydroxyl functionalities, which are able to stabilize the carbocation intermediate.

nonpolar corona and surrounding solvent to minimize the free energy of the system. Consideration of Le Chatelier's principle explains the high turnover number (17400) obtained as the substrate is driven in and the product driven out of the catalytic site. Hence the dendrimer functions as a catalytic "pump" and almost quantitative conversions can be achieved with very low catalyst loading (less than 0.01 mol%). In a related approach, acid–base catalysis has been explored by Morao and Cossío, who used a single tertiary amine at the core of poly(benzyl ether) dendrimers to catalyze nitroaldol reactions.[79]

Finally, catalytically active sites, initially located at the focal point of dendrons, have been thoroughly investigated by Fréchet and co-workers with regard to their use as macromolecular initiators.[80] This approach provides access to a new class of hybrid materials of dendritic–linear block copolymers. By choosing an appropriate initiator, a variety of monomers could be polymerized successfully. For instance, dendritic alkoxides have been employed in the ring-opening polymerization of ε-caprolactone,[80a] dendritic chlorides initiated the atom-transfer radical polymerization of styrene,[80b] while dendritic nitroxides led to the living free-radical polymerization of styrene (Figure 9).[80b] Dumbbell-like triblock materials could be obtained when a combination of a dendritic initiator and a dendritic capping group was used.[80c]

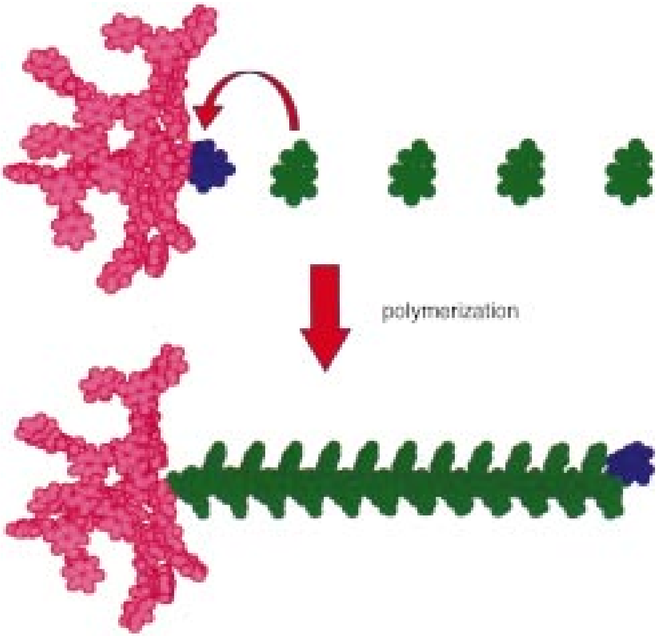


Figure 9. A fourth generation poly(benzyl ether) dendron (pink) having a nitroxide focal point functionality (blue) serves as an initiator for the living free-radical polymerization of styrene (green).[80b]

7. Outlook

Throughout this review we have focussed on the encapsulation motif utilizing dendritic building blocks. Clearly, the preparation of such materials requires great synthetic efforts, typically involving multistep procedures and chromatographic separations. In a practical sense, the whole field of dendrimer chemistry suffers from this disadvantage and alternative synthetic methods are still needed.[81, 82] Different approaches to encapsulate single active core functionalities have recently been explored and include branched star polymers[83] as well as dendritically cross-linked polystyrene based resins.[84] Furthermore, polymer-imprinting techniques have been applied to yield "cored" dendrimers having the potential to encapsulate small molecule guests resembling their template.[85] Accompanying alternative encapsulation strategies, the incorporation of new core functionalities, especially nanosized inorganic clusters, has received increasing attention. Such materials combine the unique properties of inorganic clusters with the superior processability of organic polymers. Recent efforts include, for instance, silicon dioxide core materials[86] and encapsulated quantum dots.[87] Alternatively, noncovalent methods utilizing dendrimers as hosts for nanoparticles have been explored in the laboratories of Crooks and Tomalia.[88]

The future will surely witness extensive research at the interface of inorganic chemistry and polymer science, with particular focus on such new hybrid materials. Furthermore, the synthesis of increasingly large and complex target structures through supramolecular interactions will be an important future milestone. Control over the spatial arrangement of isolated moieties will be the key to achieving new collective properties. Finally, future studies will enable us to gain more insight into the crucial role of dendrimer morphology in energy-transfer phenomena, which will ultimately lead to a better understanding of photosynthesis and the construction of new, improved systems for solar-energy conversion as well as superior light-emitting devices.

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