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The Polar Side of Polyphenylene Dendrimers

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Polyphenylene dendrimers (PPDs) represent a unique class of dendrimers based on their rigid, shape persistent chemical structure. These macromolecules are typically looked at as nonpolar precursors for conjugated systems. Yet over the years there have been synthetic achievements that have produced PPDs with a range of polarities that break the hydrophobic stereotype, and provide dendrimers that can be synthetically tuned to be used in applications such as stable transition metal catalysts, nanocarriers for biological drug delivery, and sensors for volatile organic compounds (VOCs), among many others. This is based on strategies that allow for the modification of PPDs at the core, scaffold, and surface to introduce numerous different groups, such as electrolytes, ions, or other polar species. This review is aimed to demonstrate the versatility of PPDs through their site-specific chemical functionalization to produce robust materials with various polarities.

Keywords: Polyphenylene dendrimers, polarity, nanocarrier, intermolecular interactions.

1. Introduction to polyphenylene dendrimers:

Polyphenylene dendrimers (PPDs) are highly branched, rigid, monodisperse macromolecules consisting of substituted benzene rings.[1, 2] These materials inherently have the appealing characteristics of being chemically stable and shape-persistent, yet their ability to be functionalized with nano-site perfection is often overlooked.[3] The chemical modification of these dendrimers can take place in the core, scaffold, or on the surface which offers flexibility towards targeting specific qualities.[4,5] Combining these concepts affords a rare type of material that can be tailored towards an assortment of applications through clever synthetic design.

The key to making such multi-functional dendrimers arises from the molecular tool kit employed in their synthesis, which consists of a core, scaffold, and surface building blocks (**Figure 1**). PPDs can be formed by either a divergent (palladium catalyzed coupling reaction).[6,7] or convergent (Diels-Alder cycloaddition reaction)[2,8] approach, though currently nearly all dendrimers are synthesized by the convergent growth mechanism. Thus, PPDs are synthesized through repetitive Diels-Alder cycloaddition reactions, which mean the only requirement is to have a proper diene and dienophile. This opens the door for a variety of polar moieties to be inserted at all three levels of the dendrimer, because as long as they are tolerant to elevated temperatures they can withstand the dendrimer formation.

First, a core (depicted as the gray sphere) must be chosen with two things in mind: 1) what is the desired function for the interior of the dendrimer and 2) what is its targeted geometry? Since the only requirement is to have accessible ethynyl groups (dienophile), a variety of polar functionalities can be synthesized to be the dendrimer core as will be discussed below. Specifically, it is important to observe how the bulky dendrimer arms shield the internal polar or charged core and the resulting effect on their function (*i. e.* ion dissociation, conductivity, catalyst stability, *etc*.). Additionally, the design of the core molecule will determine the geometry of the macromolecule through the number and location of the ethynyl groups, which also has a significant impact on the resulting properties of the material. It is also possible to make asymmetric dendrimers through a step wise core synthesis. Here, the core molecule must have reactive and unreactive (protected) ethynyl groups and dendrimer formation only occurs for the reactive sites. Then upon deprotection of the previously inert branching points, the other part of the dendrimer can be expanded with different molecules to form asymmetric PPDs. This concept can be extremely useful for applications such as interfacial or surface bound chemistries, as well as for the synthesis of Janus type particles. These particles are defined as having at least two distinctly different surface functionalities.[9-11] This multi-functional surface can be advantageous for doing different types of chemistry on the same particles, which can be important for the fields of self-assembly, emulsifiers, and catalysis.[12-21]

The scaffold building blocks, as illustrated as green spheres in **Figure 1**, are instrumental in tuning the polarity within the interior of PPDs. The cyclopentadienone (diene) (CP) is the essential aspect of this concept because it is the unit that reacts with the ethynyl groups from the core to emit carbon monoxide and form a benzene ring, and hence build the next dendrimer generation. It is important to note the architectures at the 2-, 3-, 4-, and 5- positions of the cyclopentadienone, because this is what incorporates desired polar groups within the scaffold (2- and 5- positions) and differentiates these molecules from those used to form the surface. The scaffold CP typically have triisopropyl (TIPS)acetylene moieties at the 3- and 4- positions, which can be deprotected upon reaction with tetrabutylammonium fluoride (TBAF) to yield ethynyl groups. Therefore, these Diels-Alder cycloaddition reactions provide

two branching points per reaction site and the molecules can be defined as A_2B monomers. These newly formed ethynyl species can then be utilized with additional building blocks to either continue to form higher generation dendrimers or to surface cap the PPDs. It is also possible to make A_4B monomers by placing TIPS-acetylene moieties at all four positions of a CP, which would then afford the opportunity to form four reactive ethynyl groups per reaction site. PPDs made with A_4B CP are denser than those formed by A_2B units due to the extra branching positions. The many different approaches to functionalize the scaffolds of PPDs will be reviewed below.

While surface building blocks (blue and red spheres) share the necessary cyclopentadienone motif with those that are used for the scaffold, it is the components placed at the 3- and 4-positions that differentiate between them. As mentioned above, scaffold repeat units have the TIPS-acetylene groups there, so that they can be deprotected for sequential dendrimer generation formation. Conversely, the molecules used for surface modification determine which polar groups are placed over the PPD surfaces. In this case, different moieties can be placed at any of the positions on the cyclopentadienone, giving rise to a variety of surface functionalizations which will be discussed towards the end of this article.

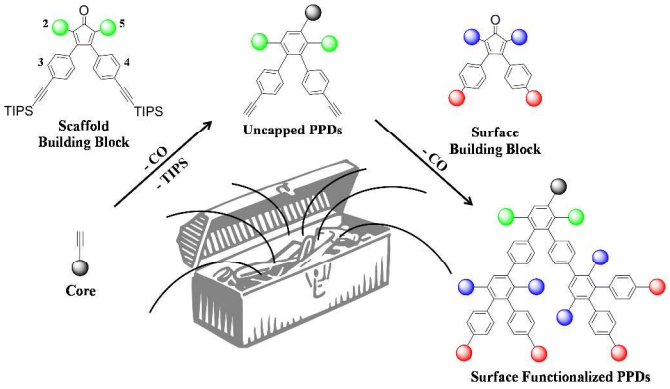

Figure 1: Illustration of the molecular tool kit for polyphenylene dendrimer synthesis.

Right now we would like to reiterate that this article will focus on PPDs functionalized with various heteroatoms, which change the polarity of the dendrimers to varying degrees. The capability to regulate a PPDs polarity from unipolar (unmodified), to slightly polar (*i. e.* addition of pyridyls, carboxylic esters, nitrophenols, *etc*), to highly polar (*i. e.* introduce ions or electrolytes) is a powerful technique for controlling the final molecular properties. This is not meant to ignore the many significant achievements of unpolar dendrimers, which can also be functionalized in an assortment of ways with unpolar groups, with some examples being shown in **Figure 2**.

These include the cyclodehydrogenation of PPDs to planarize the structures forming nanographenes (**Figure 2A**), which were some of the first reported synthesis of graphene type molecules.[2,22,23] Such well-defined nanographene structures hold tremendous potential for organic electronic and optoelectronic applications.[24-27] In this case, PPDs are typically reacted with $FeCl_3$ for the cyclodehydrogenation and planarization of the dendrimers, where the resulting dimensions of the graphene derivative are determined by the geometry and generation of the PPD precursor.[23,28,29] Furthermore, the solubility of these materials is controlled by the edge functionalities, which can be manipulated by altering the surface groups of the dendrimer. These edge moieties also influence the self-assembly of the nanographene structures into column structures in discotic liquid crystals through π-π stacking.[30,31]

There has been immense effort towards using these dendrimers in optoelectronic applications, based on the ability to incorporate units such as perylenetetracarboxydiimides, triphenylamines, and triphenylenes, among others, throughout the multilayer molecular design.[32-34] There have been many PPDs build from cores comprised of pyrene, perylenetretracarboxydiimde dyes, or iridium complexes, where the dendrimer arms can prevent aggregation of the species, while also influencing their photophysical properties like increasing their photoluminescence quantum yields or suppress triplet-triplet annihilation.[34-39] **Figure 2B** is an example of a multilayer dendrimer that has triphenyl amines on the surface and a pyrene core that acts as a blue emitter.[40] Another example was a PPD built from a terrylenetetracarboxdiimide (TDI) core that had perylenedicarboximide (PDI) and naphthalenedicarboximide (NMI) units at different distances on the surface.[33,41] This macromolecule displayed a stepwise energy transfer from the surface bound NMI and PDI groups to the core TDI, and it also was able to absorb radiation over the whole visible spectrum.

Additionally, some applications desire unpolar surfaces, which was the case for the dodecyl functionalized PPDs (**Figure 2C**) that were used to form self-assembled nanorods.[42-44] While there are numerous other ways to examples of scientifically interesting PPDs with unpolar functionalities, there have been a number of well written reviews that have already discussed these materials in detail which are highly recommended.[4, 45-47] Thus, we would like to focus this article on the cutting edge accomplishments in the field of polyphenylene dendrimers which tend to focus on a variety of polar functionalizations in an effort to eliminate the misconception that PPDs are solely a collection of fused benzene rings.

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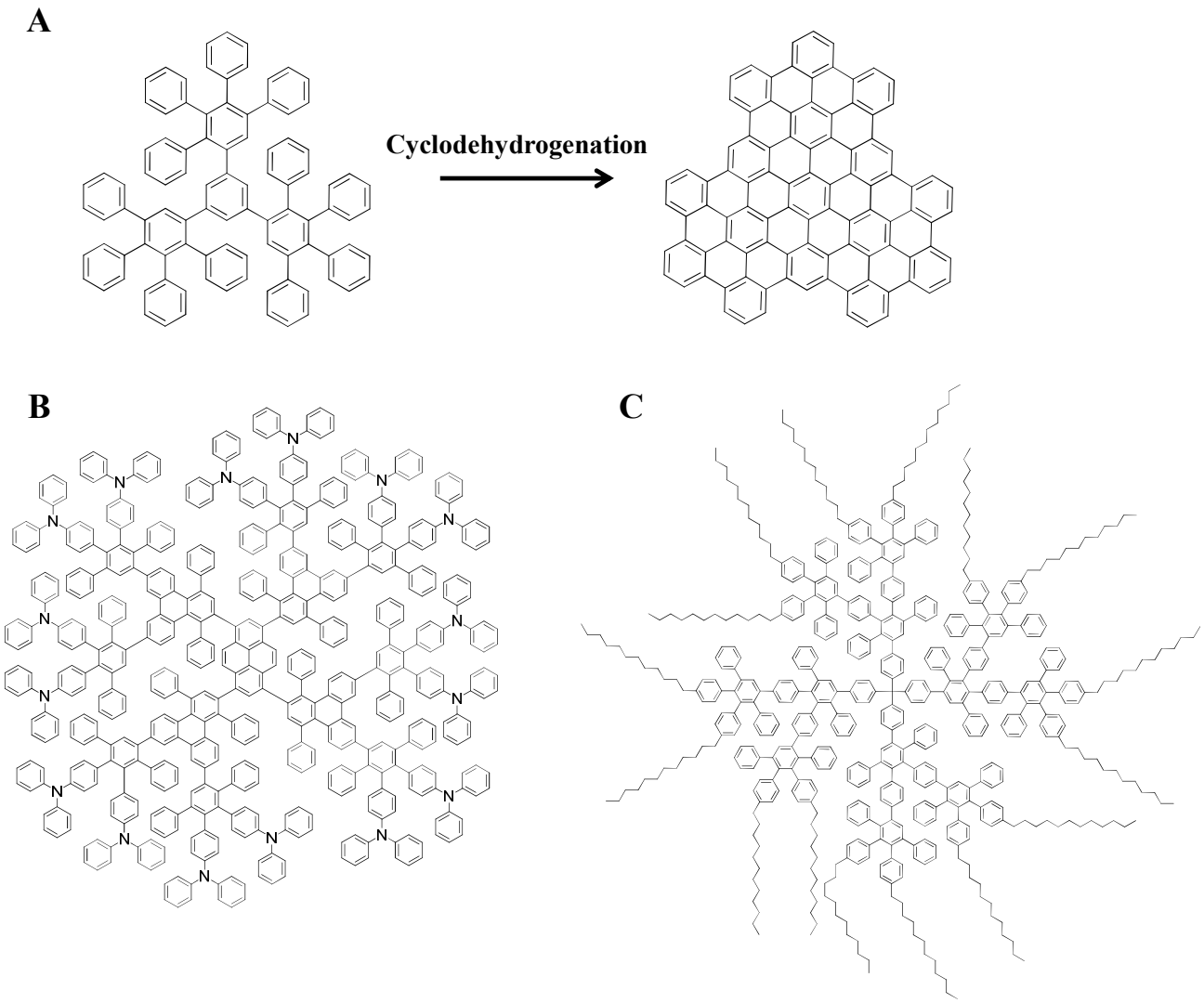

Figure 2: Chemical structures of A) PPD cyclodehydrogenation, B) blue emitting dendrimer and C) dodecyl-functionalized PPD for self-assembly applications.

2. Dendrimer core:

As stated above, a dendrimer core can be used to establish the number of arms and geometry of the macromolecule, while it can also influence the overall characteristics of the system such as photophysical properties, ion dissociation, or conductivity. For instance, a special type of core stems from charged anions (boron based) or cations (phosphorus based), where the polyphenylene dendrons shield the charges resulting in what are defined as weakly coordinating ions (WCIs). The overall ionic character of these materials is dependent on the dendrimer generation in a sense that at higher generations there is more charge shielding and thus Coulombic forces decrease. Currently, there are immense efforts towards finding less coordinating WCIs for the fields of catalysis, electrochemistry, battery technology, and ionic liquids. [48-59]

Anionic PPDs have been synthesized up to the 3rd generation from an ethynyl functionalized tetraphenylborate core, as seen in **Figure 3**, which lead to the formation of weakly coordinating anions (WCAs).[60] The boron core had to be stabilized by four electron withdrawing tetrafluorophenyl groups in order to enable the build-up for higher generations. The introduction of fluorine atoms to the inner phenylene rings caused the appearance of several conformational isomers (atropisomers), which hampered the crystallization of higher generation borate salts. Tetrabutylammonium (TBA) was initially used as the counterion given its stabilizing efficiency and solubility in a range of organic solvents. However, ion exchange techniques with various resins enable the exchange of the counterion to be different alkali and alkaline earth metal

ions, organic cations, and even other charged polyphenylene dendrimers of various generations.

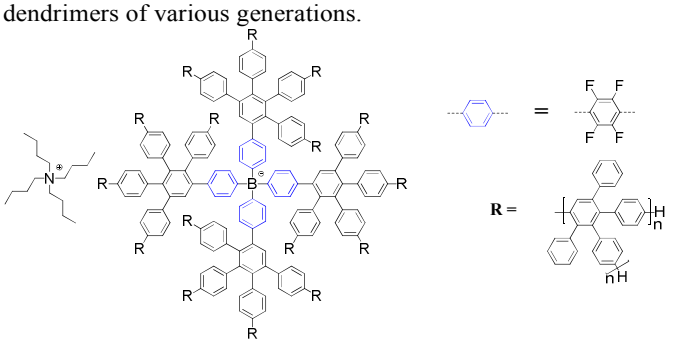

Figure 3: Tetrabutylammonium borate based PPDs.

3rd Generation borate dendrimers stabilized with TBA were found to have a diameter of ~ 6 nm, and it was observed that as the ion size increased so too did the ion dissociation in low polarity solvents. The conductivity values (borate salts of different generations and surface modifications) slightly increased with anion size despite the substantial decrease of anion mobility that accompanied the growth. Thus, reduced mobility must be overcompensated for by an increased degree of dissociation, which is attributed to a better steric shielding of the charge by the hydrophobic dendritic shell. Finally, a further enhancement of ion dissociation was observed when pentafluorophenyl- or 3,5-bis(trifluoromethyl)phenyl units were attached to the dendrimer surface (see **Figure 4**).[60] Thus, the powerful concept of dendronization is reflected by its versatile ability to tailor ion dissociation and solubility for both cationic and anionic species. The size of the PPD scaffold, the degree of branching (A_2B or A_4B growth step) as well as surface functionalization (fluorination, CF_3 decoration) can be specifically addressed in order to control electrolyte properties in organic solvents.

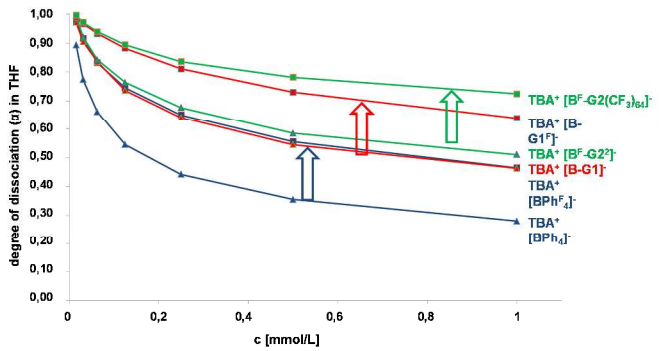

Figure 4: Degree of dissociation of different TBA^+ borate salts in THF. Ph^F = pentafluorophenyl unit; Gx = value of dendrimer generation; $(CF_3)_x$ = total number of CF_3 groups on the dendrimer surface.

The ability to tune the polarity of PPDs based anions was further exploited by the incorporation of photoswitchable azo-benzene units throughout their scaffold. It is well documented that azobenzene groups can undergo reversible *trans*/*cis* isomerizations upon exposure to 365 nm (*trans* to *cis)* and 450 nm (*cis* to *trans*) radiation.[61-65] For this reason a highly functionalized 2nd generation borate salt (**Figure 5**) was synthesized in which the ion conductivity could be altered by light.[66] In this case, when the azo-benzene units were in the *trans* configuration the dendrimer arms were fully extended resulting in larger yet less dense structures. Then exposure to 365 nm radiation induced a *trans*/*cis* isomerization which shrunk the dendrimer, and increased the shielding effect between the PPD and its counterion based on a more dense packing of the dendrons, as seen in **Figure 5**. The PPDs could transform back to the *trans* orientation upon irradiating with 450 nm light, illustrating an efficient photo-sensitive system. The size change for this isomerization was quantified by DOSY-NMR spectroscopy which determined the hydrodynamic radius of the *cis* configuration ~1.6 nm, while the radius increased to ~1.9 nm for the *trans* isomer.

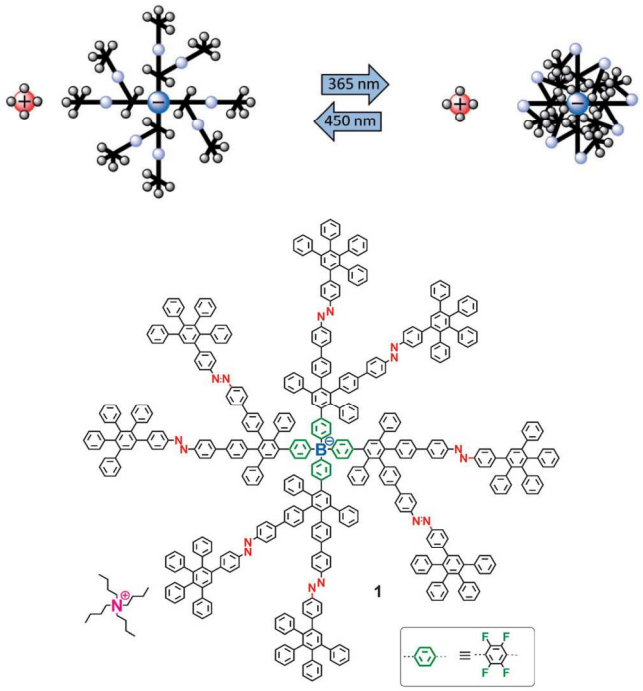

Figure 5: Illustration of size- and density switching of a rigidly dendronized anion by azobenzene photoisomerization, and the structure of borate salt X, which bears 8 azo-benzene units throughout its dendrimer scaffold. (Reprinted with permission from John Wiley and Sons (2013))[66]

The reversible transformation from *trans* to *cis* configurations had a minimal impact on the ion dissociation of these materials. Switching the PPDs from the *trans* to *cis* isomers resulted in an increase of less than ~5% in the dissociation of the dendrimer with TBA, with values between 0.64-1.01 depending on the concentration (1.5-5.0 x 10^{-4} M in THF). However, there was a more noticeable difference in the conductivity measurements between the isomers. In this case the isomerization from *trans* to *cis* forms generally resulted in a ~20-25 % increase in the molar conductivity of the dendrimers, with maximum values of 35.8 S cm^2 mol^{-1} (*trans* isomer) and 41.6 S cm^2 mol^{-1} (*cis* isomer) occurring at a concentration of 1.5 x 10^{-4} M in THF.[66] The ability to not only tailor the physical properties of these dendrimers by generation size, but also by a photo-switchable trigger represents a stimuli-responsive field of weakly coordinating anions (WCAs) that had previously been unstudied.

It was imperative to synthesize PPD weakly coordinating cations (WCCs) to complement the WCAs, thus providing a multipurpose ensemble of weakly coordinating ions. This was accomplished by encapsulating a phosphonium species in the core of PPDs through using a tetra-4-ethynylphenylphosphonium molecule to synthesize dendrimers up to the 3rd generation, as shown in **Figure 6**.[67] To the best of

our knowledge this represents the largest organic cationic molecule known, establishing it as a very important WCC.

Once PPDs with both borate and phosophonium cores were synthesized to varying generations it was necessary to conduct studies on the dissociation properties of different ion pairs. Interestingly, the systematic variation of the cation size in conjunction with the large borate anions provided the means of approaching the Bjerrum length λ_B in solvents of low polarity resulting in super-weak ion pairs.[67,68]The significance here was inspired by increasing the conductivity of these systems in nonpolar solvents. Ion dissociation in nonpolar solvents is described by the Coulomb law for two monovalent charge carriers given as:

$$E_c = \frac{e^2}{4\pi r_c e_s e_0}$$

Here, e is the elementary charge, ε_0 the permittivity of free space, r_c the distance separating a point-like cation from a point-like anion, and ε_S the dielectric permittivity of the surrounding medium. The "escape distance" from the Coulomb energy is set by the Bjerrum length, $\lambda_B = e^2/4\pi\varepsilon_0\varepsilon_S k_B T$, giving the characteristic separation between two ions at which Coulombic interactions are balanced by thermal energy.[69] These studies were carried out by elucidating the ion dissociation characteristics of different sized PPDs with either borate or phosphonium cores as illustrated in **Figure 6**.

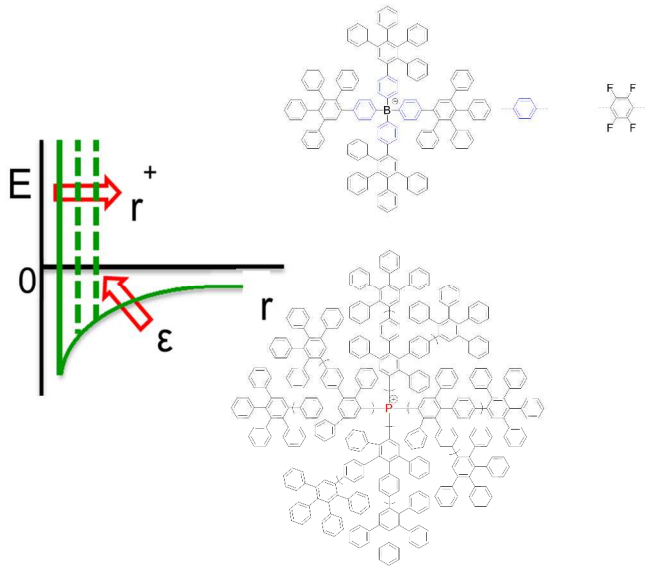

Figure 6: Structures of the dendritic molecules as a function of the cation size. All salts share the same anion, i.e., borate (B^F-G1$^-$). Monovalent and divalent ions are shown, respectively, in blue and red.
(Center) Effective Coulomb energy (green solid line) demonstrating the effect of increasing dielectric permittivity of the medium and the effect of increasing cation size (dashed lines).

For salts with small cations (Li^+ BF-G1−, Na^+ BF-G1− and K^+ BF-G1−), increasing cation size lowers the ionic conductivity, whereas the opposite trend was observed for bulky cations (P-G1$^+$ BF-G1−, P-G2$^+$ BF-G1−, and P-G3$^+$ BF-G1−). This can be attributed to the large polyphenylene dendrons that shield the phosphonium cations. As the size of the dendritic ion is increased the shielding effect of the dendrimer arms causes a decrease in ion dissociation energy. These WCI systems represent a unique balance between ion dissociation (promoted by the bulky ions) and charge transport (inhibited by the large ions), with the ability to target the desired electrolyte characteristics in solution through the use of a combination of dendronized ions and non-dendritic materials.[67]

Besides implanting ionic species into PPD cores, another area of interest is transition metal catalysts that benefit from the shielding effect of the dendrimer arms. Polyphenylene dendrons were synthesized with a pyridine unit that acted as a ligand for a palladium catalyst as depicted in **Figure 7**.[70,71] By orienting two dendrimer arms around the catalyst it sterically shielded the active sites between neighboring molecules, and thus prevented them from reacting to form palladium black which results in catalyst failure.[72] These materials were used as catalysts for the aerobic oxidation of alcohols, where the dendronized catalyst maintained its activity and solubility during the process, while palladium catalysts without the arms precipitated due to palladium black formation.[70] Hence, introducing dendrimer arms as ligands for transition metal catalysts through polar pyridine groups allowed them to maintain their activity. This represents a new class of stable catalysts through the utilization of functional PPDs acting as shielding ligands.

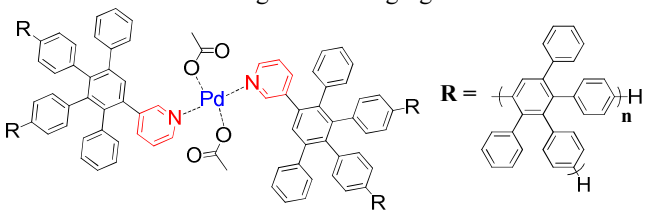

Figure 7: Palladium catalyst with PPD ligands.

Another example of placing a transition metal catalyst into the core of PPDs came from functionalizing cyclopentadienyl(dicarbonyl)cobalt with accessible ethynyl groups, which then underwent Diels-Alder reactions with cyclopentadienones to build polyphenylene dedrons around the catalyst (**Figure 8**).[73] In this case, four dendrimer arms were coordinated to the cobalt species that resulted in the stabilization of the electro-active 17 electron state. This process increased the oxidation potential of the system up to 0.83 V based on the stabilization from the bulky dendrons, and produced an active cobalt species that was stable to air and water.

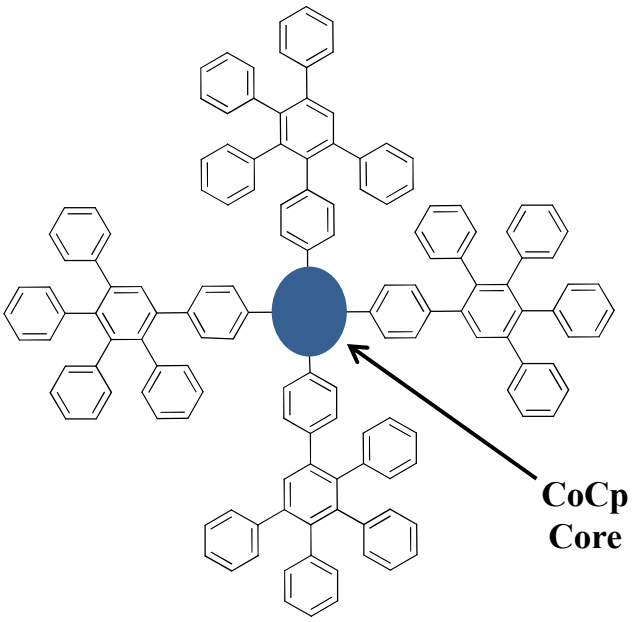

Figure 8: Cobalt catalyst surrounded by four 1st generation PPD arms.

It was also possible to incorporate cobalt as the core for PPDs through the use of the more polar metallophthalocyanine (MPc) based dendrons as ligands, as shown in **Figure 9**.[74] This led to 1st generation dendrimers with 4 arms that were able to stabilize the cobalt core, and this process provided an avenue to tune the solubility of the complexes. In particular, it became possible to disperse these PPDs in polar solvents where the dendrimers arms prevented aggregation of the cobalt that was observed for other complexes. Furthermore, the steric shielding of the dendrimer arms limited the axial coordination selectivity of the cobalt core, specifically for different sized pyridine derivatives. These complexes proved to be viable chemosensors through the uptake of small guest molecules. Here, when the PPDs were exposed to various gaseous analytes there were observed changes in their absorption and fluorescence characteristics based on interactions between the guests and MPc cobalt core.

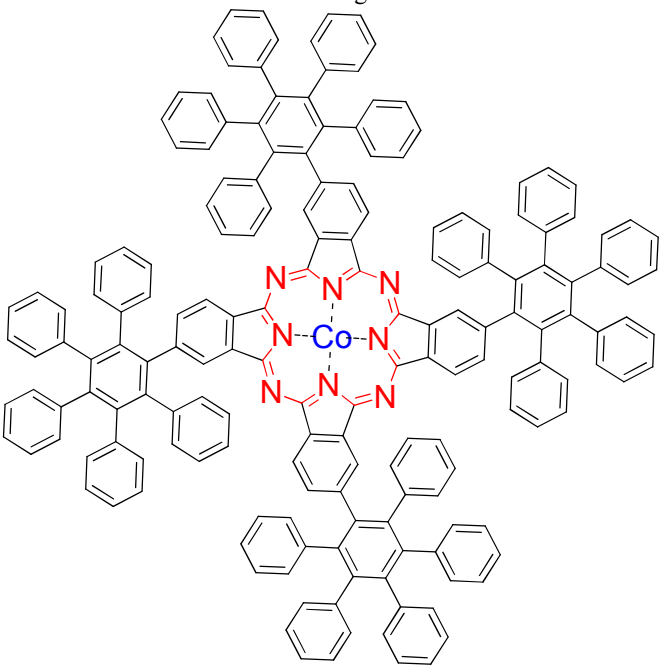

Figure 9: Cobalt catalyst surrounded by metallophthalocyanine based dendrons as ligands.

As previously mentioned, a key property of the dendrimer core is its ability to determine the number of arms and the geometry of the resulting macromolecule. A unique aspect of introducing functional transition metals as the core is the potential to achieve complex geometries based on the chosen metal and ligand structures. For example, bipyridine based polyphenylene dendrons were used as ligands for asymmetric, cationic ruthenium complexes that had an octahedral geometry (**Figure 10**).[75] The 3rd generation dendrons were able to stabilize the charged ruthenium core, while the geometry was determined by the number of arms that were coordinated to the ruthenium through ligand exchange with 4,4-bis(TIPS-ethynyl)-2,2'-bipyridine units. This approach achieved large, asymmetric PPD cations that were used to study salt properties with counter anions of different sizes. Additionally, the reactivity of the charged ruthenium core could be controlled based on the ratio of 4,4-bis(TIPS-ethynyl)-2,2'-bipyridine or PPD functionalized bipyrines, which is quite rare for ruthenium based catalysts.[76-80]

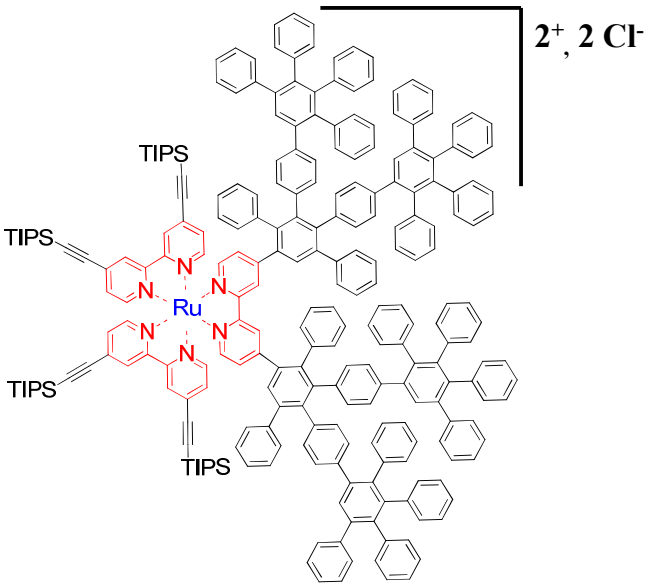

Figure 10: Asymmetric ruthenium catalyst with PPDs ligands.

3. Polar scaffolds:

While the core primarily determines the number of arms and geometry of PPDs, the scaffold can be used to tune the polarity of the dendrimer cavity, specifically towards tailoring interactions with guest species. Typically PPDs are assumed to have nonpolar voids owing to the many benzene rings of the architecture, but this ignores the creative synthetic approaches that have been implemented when addressing structural objectives.

For instance, 3rd generation PPDs were synthesized with 12 carboxylic acids placed throughout their scaffolds that provided a polar environment for guest molecules, while the surface was covered with unfunctionalized phenyl rings (**Figure 11**).[81] The functional cavities were shown to be able to encapsulate polar guest species, specifically proflavin hydrochloride, through possible hydrogen bonding that had never been previously seen for PPDs. This process led to the uptake of 3-4 guest molecules per dendrimer, and afforded a pathway to transport highly polar small molecules into hydrophobic media, illustrating a valuable approach to versatile encapsulation in different solvents.

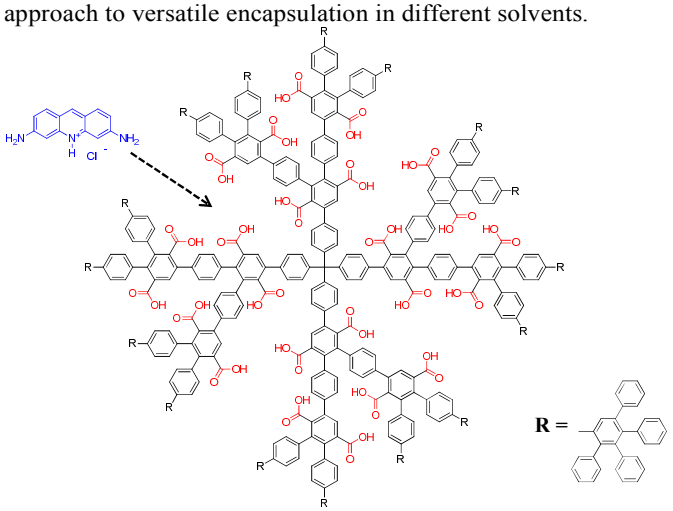

Figure 11: PPDs with carboxylic acids oriented in their scaffolds for encapsulating proflavin hydrochloride

The cyclopentadienone is the building block of PPDs, and through them it is possible to tailor the functionalities in the dendrimer scaffold or on its surface. It is possible to accomplish

this as long as the CP is available for the Diels-Alder cycloaddition reaction, meaning that a range of polar groups can be placed at the 2, 3, 4, and 5- positions on the ring, which are then inserted into or on top of the dendrimer. Through this approach PPD scaffolds have been synthesized with units that range in polarity from unpolar (pyrene, benzene) to higher levels of polarity (4-nitrophenol, 4-cyanobenzene, or N,N-dimethylformamide), illustrated in **Figure 12**.[82] In this case the dendrimers were then surface capped with phenyl groups that led to PPDs with polar scaffolds that were still soluble in nonpolar solvents. This yielded unique structures that could be loaded with polar guest molecules (benzaldehyde, 4-nitrobenzene, N,N'-dimethylformamide) and then transferred to a range of organic solvents.

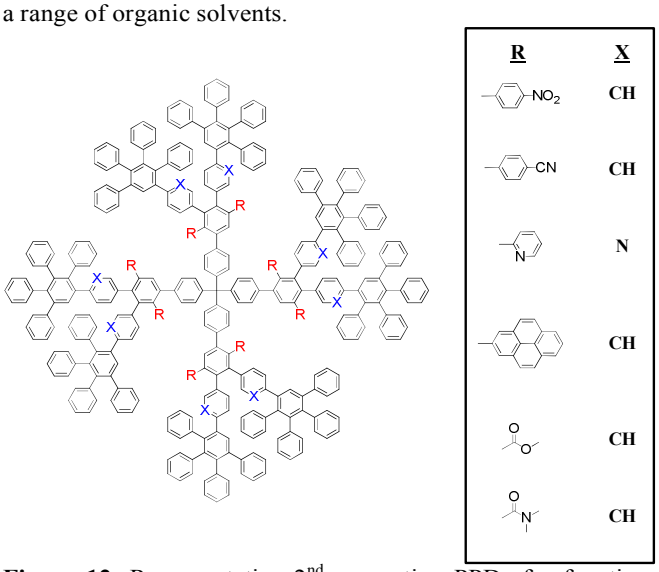

Figure 12: Representative 2nd generation PPDs for functional guest/host interactions.

When talking about encapsulation of small molecules it is important to think about the application, and how efficient a system is for a specific process. An excellent example of the need for highly efficient host systems is in the field of detectors, where the detection improves with the sensitivity of the assembly. This is even more important when investigating the detection of delicate substances such as explosives, for which the detector must be extremely accurate and able to sense even the smallest amount of material. It was found that introducing polar groups within the scaffolds of PPDs made them able to detect triacetone peroxide (TATP), a well-known and highly dangerous explosive.[82-87] 4th Generation PPDs were functionalized with 56 pyridyl units throughout their scaffolds and coated onto a quartz crystal microbalance (QCM) detector (**Figure 13**). It was necessary to calibrate the devices to differentiate between the targeted TATP and materials used for its synthesis (acetone and hydrogen peroxide). Then a nitrogen flow enriched with TATP was passed over the dendrimer coated QCM. The interaction between the pyridyl moieties and TATP afforded this system an extremely high affinity for molecular uptake with detection limits as low as 0.1 ppm concentration. The ability to fabricate a TATP detector with such sensitivity highlights the efficiency of guest/host interactions with functionalized PPDs.

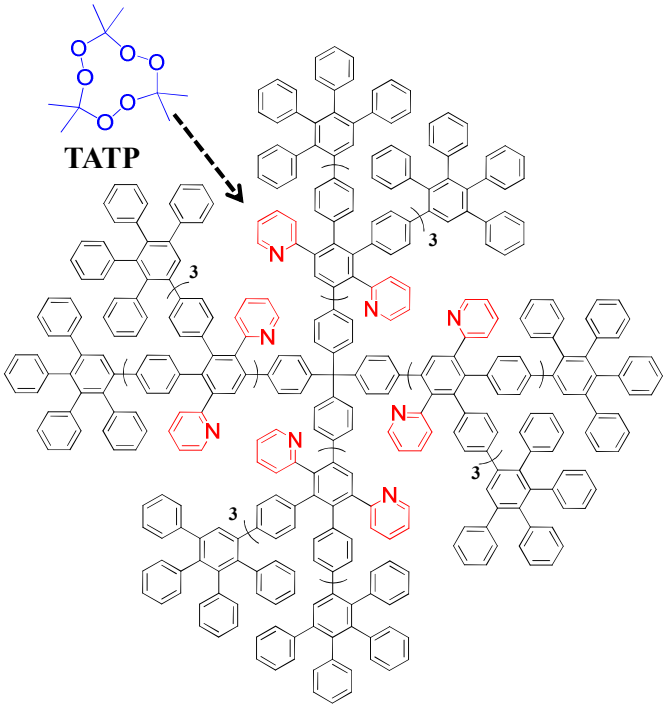

Figure 13: Pyridine functionalized PPDs for the detection of TATP.

It was important to understand the driving forces for interactions between guest molecules and PPDs, and this was characterized through isothermal titration calorimetry (ITC) analysis.[88] In this case, there is a significant difference between these studies and the PPD based QCM sensors in that molecular uptake for the detectors occurred in the gaseous state and the ITC experiments involve encapsulation of guest species in various solvents. Therefore, this approach looked at the thermodynamic interactions between the host (PPD) and guest species to determine the enthalpic or entropic influences of encapsulation in solution. For the uptake of unpolar guest moieties, such as benzene or toluene, into unfunctionalized PPDs it was found that the release of solvent molecules and their exchange with incoming guests was entropically driven (**Figure 14**). When PPDs were made to have polar scaffolds (*i.e.* carboxylic acids, nitriles, nitrobenzenes) and loaded with polar groups (acetonitrile, diethylamine, nitromethane, *etc.*) the encapsulation process was determined by enthalpic influences, typically hydrogen bonding or π-π interactions. These studies were instrumental towards the understanding of how functional scaffolds can interact with guest species, as well as how to tune the dendrimers in a manner to control the encapsulation of various guest substituents.

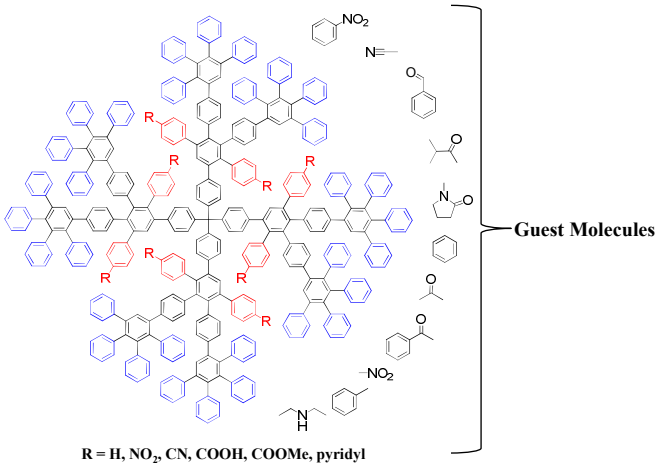

Figure 14: Functional PPDs and small molecules used for ITC encapsulation studies.

In an effort to enhance the stability of PPD based guest/host structures azo-benzene functionalities were introduced into the dendrimer scaffold. These groups have been previously mentioned, and their utility comes from their ability to undergo a reversible *cis-trans* isomerization upon irradiation at 450 nm (*cis-trans*) or 365 nm (*trans-cis*) (**Figure 15**).[89] Additionally, pyridyl units were placed throughout the scaffold to increase the polarity of the cavities to promote the encapsulation of guest molecules. "Open" PPDs (trans- isomer) were loaded with *p*-nitrophenol units and upon isomerization to the cis structure an average of two guest molecules were sterically sealed per dendrimer. These guest/host assemblies were stable through multiple precipitations and washings, and the encapsulated molecules were only released upon isomerization back to the *trans* structure. This was a formidable example of the stable uptake and release of small molecules from a host that had a controlled trigger for the expulsion of the guest, which was provided through the clever synthesis of highly functional PPDs.

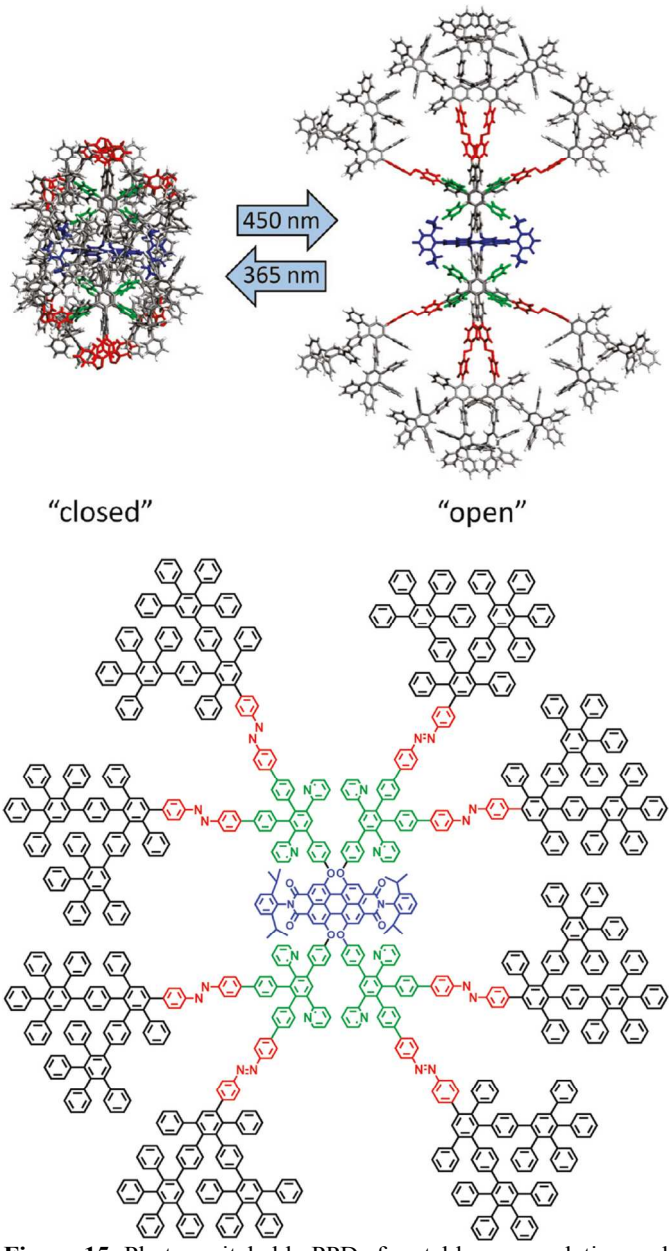

Figure 15: Photo-switchable PPDs for stable encapsulation and release studies with small molecules. (Reprinted with permission, copyright 2012, American Chemical Society)[89]

A different approach to using PPDs as hosts for guest molecules came from the incorporation of thiols into their scaffolds. This achieved two purposes, the thiols increased the polarity of the dendrimer cavities to encourage functional guest species to enter them, while they could also be used to form disulfide bonds with guest molecules to covalently attach them to the structure (**Figure 16**).[90] 2nd generation PPDs were synthesized with 8 free thiols throughout their scaffold, and when the dendrimers were exposed to a thiol-functionalized nitrophenol derivative it was observed that each PPD covalently bound 4 guest molecules to its scaffold. This conjugation is appealing because it provided an extremely stable macromolecular assembly, where the guest molecules could be released under reductive conditions, a triggered mechanism. The ability to covalently bond guest molecules to a macromolecular transport system to yield stable materials, which happen to have a highly efficient mechanism for the

release of the species, is an attractive contribution to the field of dendrimer/small molecule conjugations.

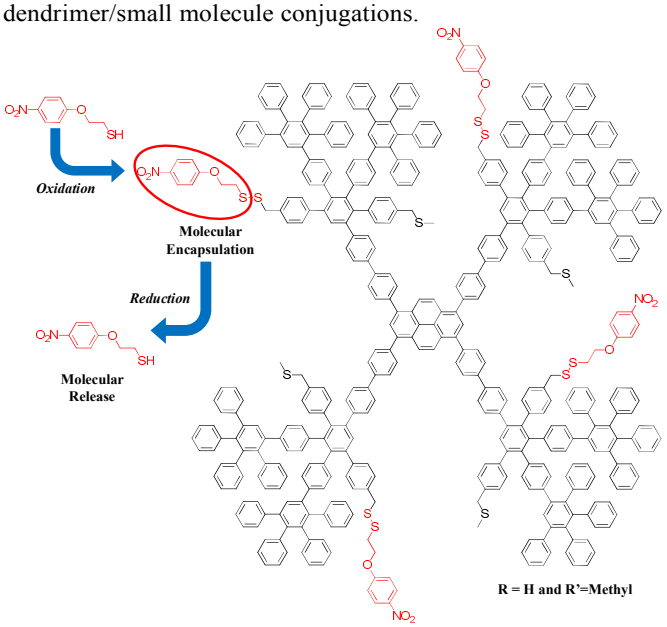

Figure 16: Reversible small molecule conjugation to PPDs functionalized with thiol groups. (Reproduced with permission from the Centre National de la Recherche Scientifique)[90]

4. Scaffold and Surface Functionalization:

The surfaces of PPDs play crucial roles in their solubility and polarity. Therefore, it is very important to tune the chemistry of the building blocks towards the desired application. It is also possible to introduce similar polar groups within the scaffold and on the surface to provide a comprehensive functionalization. One such example was done where sugar units were placed between the 1st and 2nd generation of PPDs, as well as on the surface to achieve a macromolecular structure that resembled the active center in naturally occurring enzymes (**Figure 17**).[91,92] This approach led to twenty four d-glucopyranosyl trichloroacetimidate based units being integrated throughout the 2nd generation PPD, which increased the polarity of the "glycodendrimer" structure. These materials were soluble in weakly acidic aqueous solutions or polar solvents, such as DMSO. It was shown that the dendrimers were capable of encapsulating a fluorescent probe (ANS) based on interactions (H-bonding) between the guest molecule and the sugars in the dendrimer cavities. There was an observed hypsochromic blue shift in the emission from the dye as a result of suppressed non-radiative relaxation when encapsulated within the dendrimer scaffold.[93]

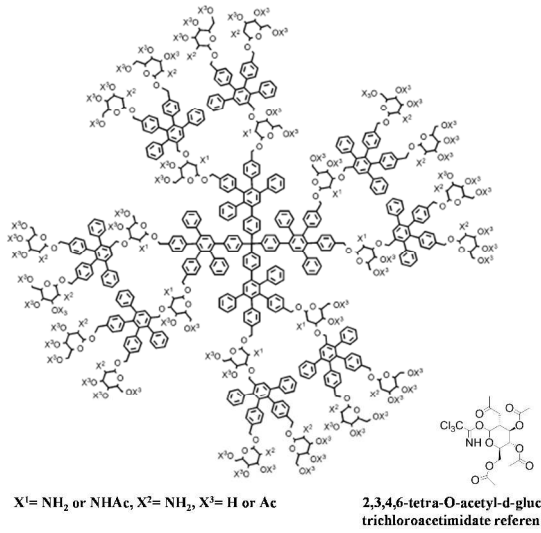

Figure 17: PPDs with sugars oriented throughout the scaffolds and on the surfaces. (Reprinted with permission, copyright 2004, American Chemical Society)[91]

Another example of tailoring the overall structure of PPDs was achieved by introducing pyridine units throughout the dendrimers, which were subsequently alkylated to produce water soluble polycationic structures, as seen in **Figure 18**.[94] 2nd through 4th generation PPDs were synthesized and mixed with poly(styrene sulfonate) (PSS) or DNA complexes to study the interactions between the charged polymer ions. By changing the relative size of the dendrimers and PSS, along with the relative charge ratios (*i. e.* pyridinium:sulfonate groups) it was possible to control the overall size of the assemblies. For small molecular weight PSS (DP between 19-78 units) mixed with the PPDs (1st or 2nd generation) it was found that aggregates (sizes up to 30 nm) were observed, while larger PSS (DP = 316 units) mixed with the dendrimers formed complexes between 6-8 nanometers depending on the dendrimer generation. This process enabled the formation of water soluble, polyelectrolyte nanoparticles with variable sizes based on polymer chain lengths and the number of incorporated charges.

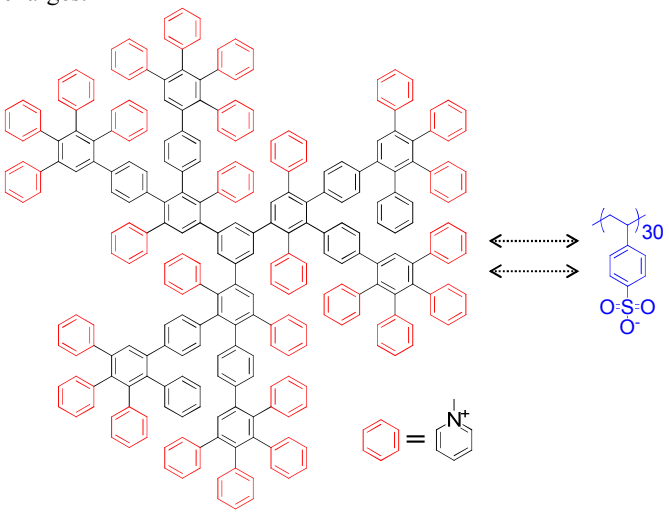

Figure 18: Cationic PPDs associated with PSS as the counterions.

As mentioned above, PPDs have been used as the active layer in QCM detectors because the rigidity of their polyphenylene backbone provides voids in their structure which can trap guest molecules. This property was first exploited when 2nd generation dendrimers were surface functionalized with polar groups (*i.e.* carboxylic acids, nitriles, or diphenylmethyleneamines) and coated onto a QCM.[95] These sensors were exposed to different volatile organic compounds (VOCs) in the gas phase, and each dendrimer was able to encapsulate up to ~5 x 10^{15} polar molecules (acetophenone, aniline, benzonitrile, or nitrobenzene), as characterized by Positron Emission Tomography (PET).

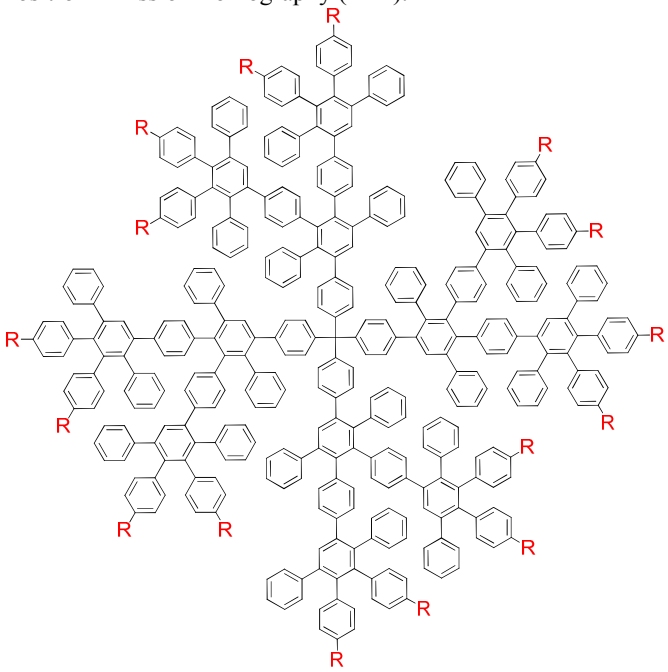

Figure 19: 2nd Generation PPD with polar surface functionalities.

There are applications where having a difference in polarity between the scaffold and surface can be utilized. Typically, PPDs have unipolar scaffolds owing to the copious number of phenyl rings, while the surface can be functionalized with a range of polar groups. One such example came from the "a posteriori" basic hydrolysis of surface bound cyano- groups on 2nd generation PPDs to form 16 highly polar carboxylic acids around the dendrimers (**Figure 20**).[96] These macromolecules were exposed to different concentrations of cyanine dye pinacyanol to study where the dye oriented (on the surface or within the dendritic voids) with the structures as characterized by single-molecule spectroscopy (SMS). Through this method it was found that at low concentrations the dye entered the scaffold cavities of the dendrimers (2 per dendrimer), while at higher concentrations dye molecules formed ion pairs with the surface bound carboxylic acids. Hence, it became possible to control the orientation of guest molecules around or inside of dendrimers based on concentration and difference in local polarities.

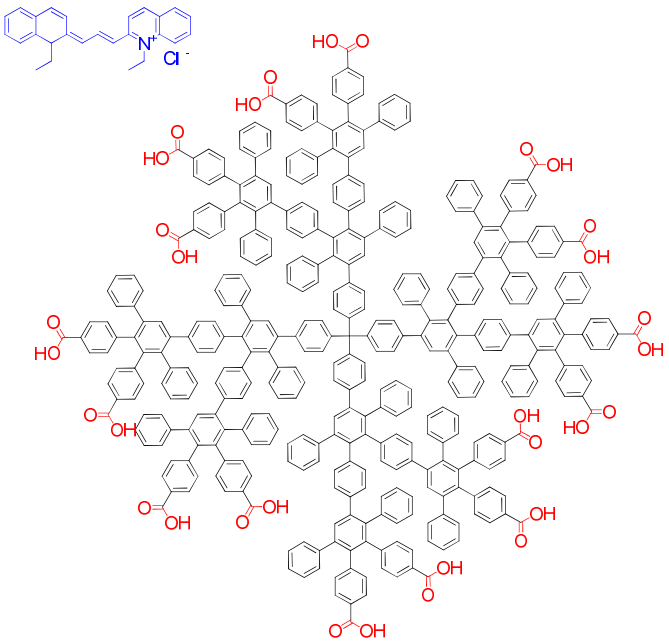

Figure 20: Carboxylic surfaced functionalized PPDs for interaction with guest species.

Introducing polar groups on the surface of PPDs can provide an efficient method to tune the solubility and function of the dendrimers. It was possible to create water soluble PPDs that resemble surface functionalized organic nanoparticles through "a posteriori" atom transfer radical polymerizations (ATRP) from the dendrimer surface. Here, 2nd generation PPDs were synthesized with surfaces functionalized with 2-bromo-2-methylpropionic esters that were used for the surface initiated ATRP of 2-tert-butoxycarbonylaminoethyl methacrylate. The t-boc groups were deprotected to the resulting amines (**Figure 21**), which demonstrated the ability to efficiently complex with DNA and plasmid DNA fragments even at low concentrations.[97] This process could be controlled by changing the number of amine groups through varying the degree of polymerization during the ATRP reaction. Interestingly, these complexes could be disturbed by exposure to sodium chloride at concentrations higher than 1 M, achieving stimuli-responsive assemblies. Furthermore, it was possible to introduce perylene diimide derivatives into the dendrimer core of these structures, which could act as a fluorescent tag for *in vivo* studies. It was found that the PPDs were able to act as a stain in the extracellular matrix (ECM) in animal tissue at physiological pHs, while introducing cationic species on the dendrimer surface provided an avenue to achieve efficient transport through cell membranes.[98,99] This method proved to be extremely valuable towards the synthesis of water soluble, core shell dendrimers where the solubility and interactions in biological media could be controlled through the "a posteriori" functionalization of the surface bound polymers.

These dendrimers have recently been studied as complexes with different RNA strains for gene expression. Specifically, the dendrimer was complexed with a RNA strain that targets the mid-gut chitinase gene (CHT10-dsRNA) in the Asian corn borer (one of the most prominent pests of corn). These assemblies were efficient at suppressing the developmental gene expression in the insects, eventually leading to their death. One of the most significant developments concerning this topic was the ability to administer the PPD based RNA to freshly hatched larvae and observe that it prevented their natural

growth, which represents the first reported complex to be orally given to insects that could provide control over certain gene expression.[100] Another advantage of this system is its non-viral gene therapy approach, while it provides an avenue towards insect control without the need for harsh chemical insecticides.

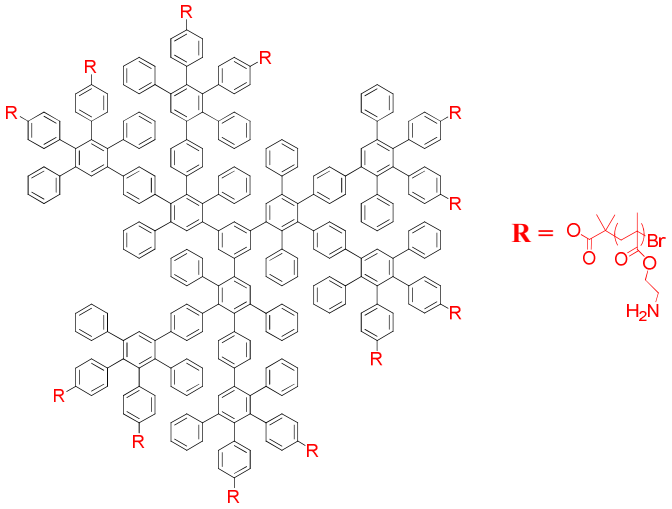

Figure 21: Core shell PPDs with surface initiated poly(2-aminoethylmethacrylate) chains.

The "a posteriori" functionalization of 2nd generation PPDs *via* surface initiated ATRP was expanded to the synthesis of diblock copolymers in an effort to form amphiphilic dendrimers. Poly(2-hydroxyethyl methacrylate) (PHEMA)-b-polystyrene (PS) was synthesized from the dendrimer surface to yield a "multicore shell" particle that exhibited unique solubility properties based on rearrangements of the polymer arms depending on their environment (**Figure 22**).[101] It was found that the hydrodynamic radius of the PPDs could shrink from 15.6 nm when the polymer arms were fully solvated to 8.5 nm upon exposure to a poor solvent for the PS (i. e. 5 vol. % methanol in THF). This was justified by the PS outer shell collapsing into the PHEMA layer to escape the unfavorable methanol solvent, essentially displaying a stimuli-responsiveness to the solvent conditions. Samples were also made to have the outer layer be the PHEMA block with the PS directly attached to the dendrimers, which could then show responsiveness to solvents that are unfavorable for the PHEMA block. The use of diblock copolymers afforded the PPDs unique amphiphilic characteristics through the "multicore shell" approach.

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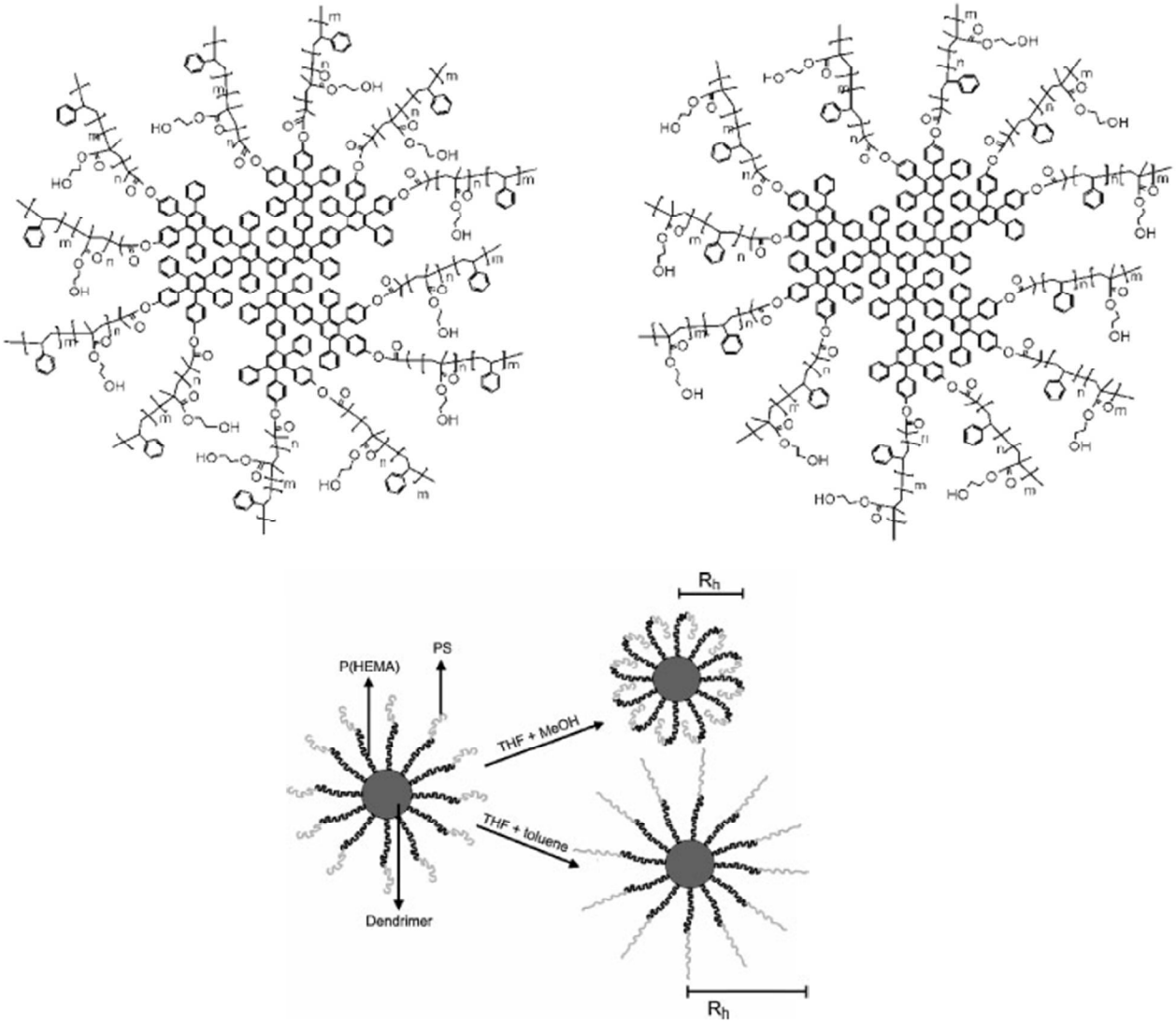

Figure 22: PPDs with surface functionalized PS-b-PHEMA arms. (Reprinted with permission from John Wiley and Sons (2007))[101]

Other benefits to introducing polarity (carboxylic acids) into "multicore shell" PPDs came from their use as templates for mesoporous metal oxides. In this case, PPDs were "a posteriori" functionalized with 12 PS-block-poly(acrylic acid) (PAA), and the PAA block was loaded with titanium oxide (TiO_2) nanoparticles (**Figure 23**).[102, 103] It was then shown that the hydrophobic PPD support and PS block could be degraded by hydrolysis, condensation, and calcination to leave a hollow sphere or ring shaped structure of the PAA loaded with the nanoparticles. The size of the dendrimer and PS block determined the pore size, while the size of the PAA block determined the shell thickness of the resulting assemblies. This represents a cute method for the formation of mesoporous metal oxide structures with a control mechanism over their dimensionality, which has applications in photocatalysis, gas sensors, and lithium ion batteries. [104-108]

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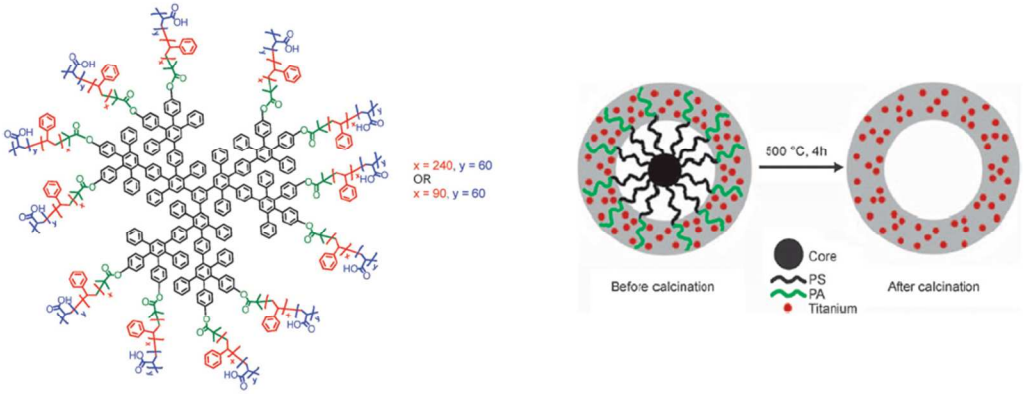

Figure 23: Core shell PPDs for the formation of mesoporous metal oxide structures. (Reprinted with permission from John Wiley and Sons (2008))[102]

A different concept towards the formation of metal assemblies assisted by PPDs involved the formation of multilayered structures of gold nanoparticles on silicon substrates. Here, polyphenylene dendrons were functionalized with an alkyl thiol, which was used as a ligand for gold nanoparticles (**Figure 24**).[109] Poly(ethyleneimine) (PEI) was deposited on a silicon surface, followed by poly (4-vinylbenzyl azide) (P4VBA)-block-PAA which attached to the surface through Coulombic interactions. The gold nanoparticles functionalized with the PPD dendrons were then covalently attached to the surface bound azides through "click chemistry." The side of the nanoparticles with free ethynyl groups was reacted with a new batch of the P4VBA-b-PAA polymer, and sequentially a layer by layer assembly of gold nanoparticles was produced. The size and shape of the layers could be tailored through the shape and size of the dendrons, while the stability of the structures was determined through the number of active azide units in the diblock copolymer. This yielded a novel method to form nanometer thick multilayers of gold nanoparticles.

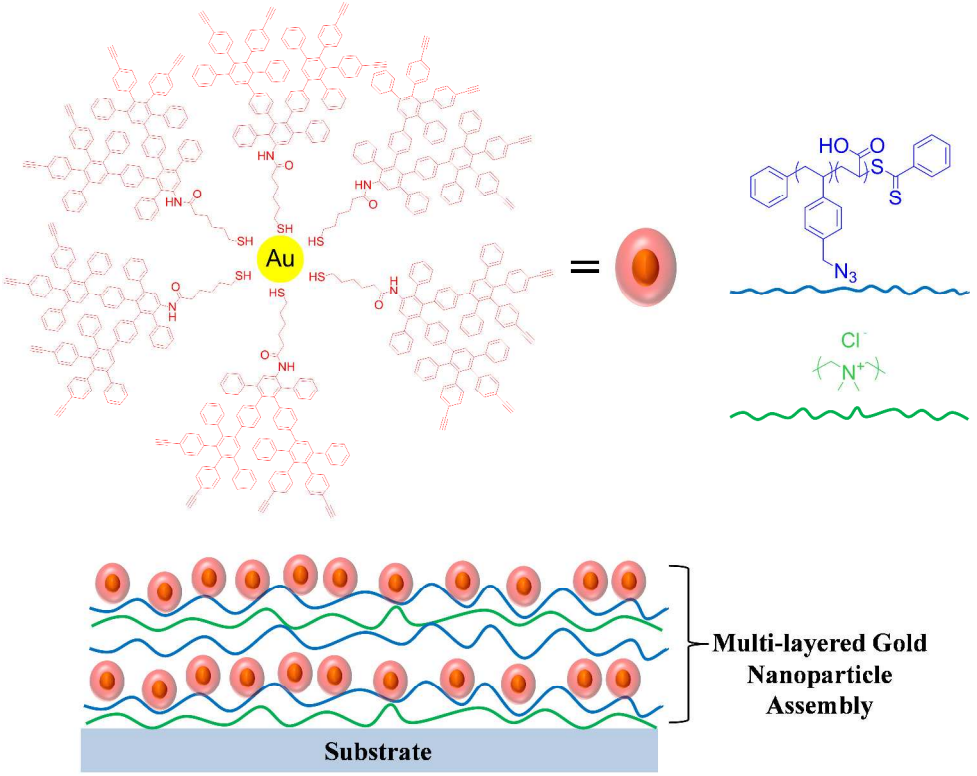

Figure 24: Multi-layered gold nanoparticles and polymer films utilizing PPD ligands.

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The photophysical properties of organic dyes can be manipulated through interactions with nanoscopic metal through plasmonic gap resonances.[110-115] This can be a difficult concept though based on the ability to orient such dyes between metallic objects on such small length scales.[116-120] One approach that proved successful was to incorporate a PDI dye into the core of 2nd generation PPDs, and then surface functionalize the dendrimers with 16 dithiolane units, which showed high affinity for silver. These structures were oriented between a silver plate and silver sphere (see **Figure 25**), which provided an avenue to achieve dendrimer thick layers on the order of 3 nm.[121] Such a sphere-on-plane (SOP) geometry was ideal for producing dendrimer layers in which the fluorescence from the PDI was quenched on the silver plane, yet amplified by ~1000 times on the silver sphere *via* plasmonic resonators.

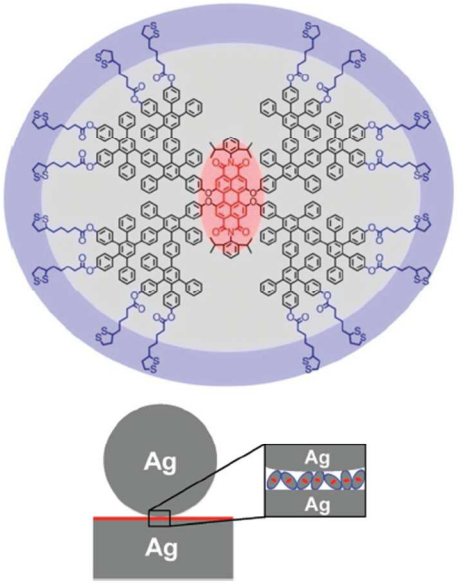

Figure 25: PPDS surfaced functionalized with dithiolanes acting as a lubrication layer between a silver plate and sphere. (Reprinted with permission, copyright 2010, American Chemical Society)[121]

Furthermore, PPDs that possess surface bound dithiolane or thiomethyl groups express a high affinity for gold nanoparticles. Mixing PPDs with surface based thiomethyl species and gold nanoparticles led to the formation of stable composites. Upon evaporation of the solvent the rigid dendrimers promote the aggregation of the nanoparticles to yield a cross-linked assembly, and this led to a facile method to form gold nanoparticle based composites. Such materials can be used as the selective layer in chemiresistor based sensors for VOCs (**Figure 26**).[122-124] In this case the PPDs cross-link the gold nanoparticles, stabilize the active layer, and increase the sensitivity of the sensor towards VOCs; while the gold nanoparticles provide good signal transduction. These devices were efficient at detecting organic solvents, such as toluene and trichlorobenzene, while having negligible sensitivity to humidity, a necessity for most sensing applications.

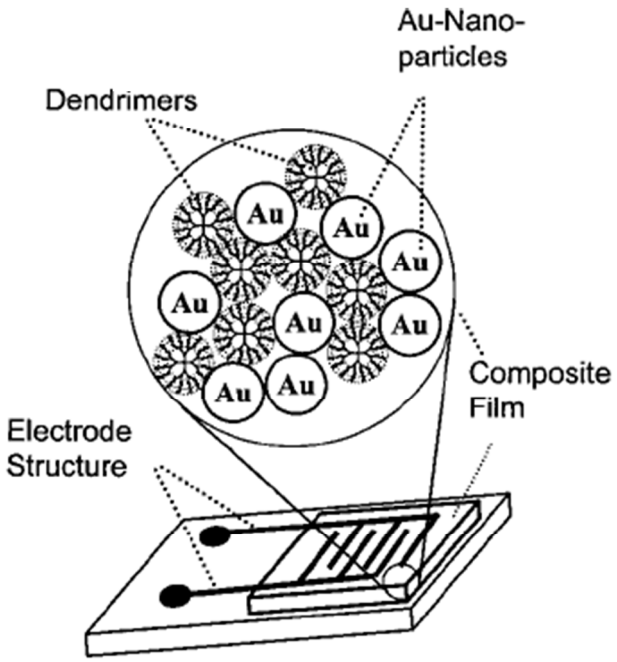

Figure 26: PPDS and gold composites as the active layer in a detector. (Reprinted with permission from John Wiley and Sons (2002))[124]

A different approach to assemble PPDs through their surface functionalization was to introduce perfluorinated phenyl rings, an example of investigating different types of polarity on a dendrimer. In this case, 2nd generation PPDs were asymmetrically functionalized where half of the surface was occupied with unmodified phenyl rings while the other half was fluorinated phenyl rings (see **Figure 27**).[125] This was one of the first examples of a Janus type dendrimer where the quantity of phenyl and fluorinated phenyl moieties could be controlled through the asymmetric synthesis. Through tuning the fluorophilicity of the PPDs it was possible to self-assemble the macromolecules into micrometer long nanofibers on highly oriented pyrolytic graphite (HOPG).[126] The driving force was attributed to the π-π interactions between fluorinated and non-fluorinated phenyl rings, and the resulting nanofibers were highly ordered.

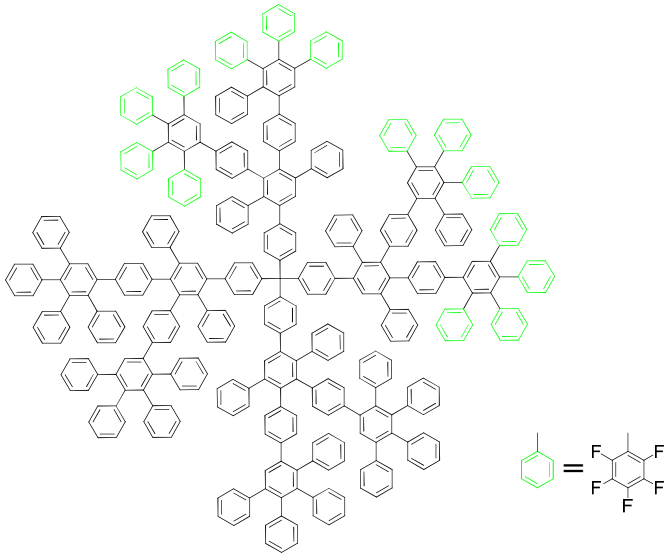

Figure 27: Fluorine surface functionalized PPDs.

The asymmetric functionalization of PPDs with polar species also opens the door for more complex fields of chemistry such as interfacial interactions, surface attached thin films, and a variety of others. Again, it is the fundamental synthetic approach to form PPDs from cyclopentadienones that can be functionalized in a variety of manners that allows for such asymmetric growth. For instance, 1st generation PPDs were surface made with three perylenemonoimide dyes and a single biotin unit, which could act as an anchor point on foreign surfaces or structures, as shown in **Figure 28**.[127] When this dendrimer was mixed with Tween 20 detergent the structure became water soluble, providing an aqueous perylenemonoimide dye. Moreover, this PPD was able to specifically bind to the protein streptavidin through the biotin unit, which led to the ability to fluorescently tag the protein.

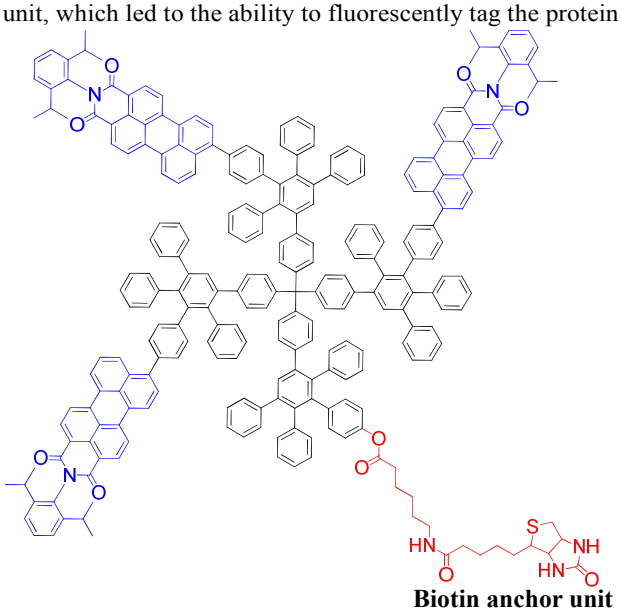

Figure 28: Asymmetrically functionalized PPDs for protein binding.

The concept of asymmetric PPDs was expanded to include other polar groups such as amines, carboxylic esters, or alkyl chlorides that can act as an anchoring group for either attachment to another structure or for post-dendrimer formation functionalization. The other surface sites could then be synthesized to have either nonpolar (typically benzene rings, TIPS-acetylene) or polar groups (amides, diphenylmethylamines, carboxylic acids, *etc*) based on the desired application (*i.e.* surfactants, surface attachment, or protein binding). This highlighted the capability to incorporate multiple functionalities onto PPDs to tune their polarity (**Figure 29**).[128]

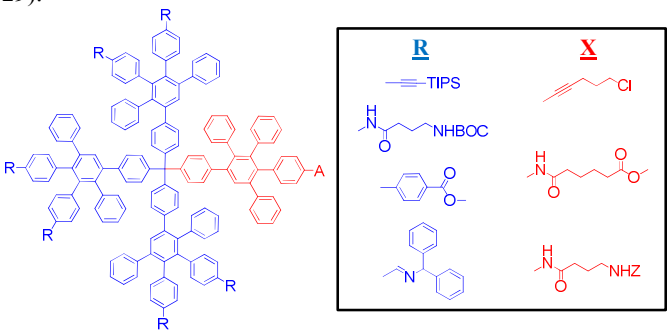

Figure 29: PPDs asymmetrically modified with different polar groups.

Biological applications (*i.e.* cell uptake, nanocarriers for therapeutic drugs, complexes for gene expression) are a field that most do not think PPDs should be relevant to based on hypothetical effects of the benzene rings that make up the dendrimers. However, through the many ways to modify these materials it has become possible to introduce PPDs in a range of biological settings. For example, 1st and 2nd generation PPDs were surface functionalized with amine groups which were then coupled to the C-terminus activated carboxylic acid groups of poly(L-lysine) (**Figure 30**).[129, 130] The attachment of the peptides to the dendrimer surface made the materials soluble in aqueous media and promoted their biocompatible. Moreover, the length of the poly(L-lysine) determined the self-assembly of the dendrimers where small or large peptide lengths led to undefined mixtures of α-helical and β-sheet structures, while intermediate lengths produced primarily α-helical assemblies.[131] This process was important towards producing polar PPDs that were water soluble and biocompatible, and the ability to regulate the self-assembly process through controlling the peptide chain length was advantageous as well.

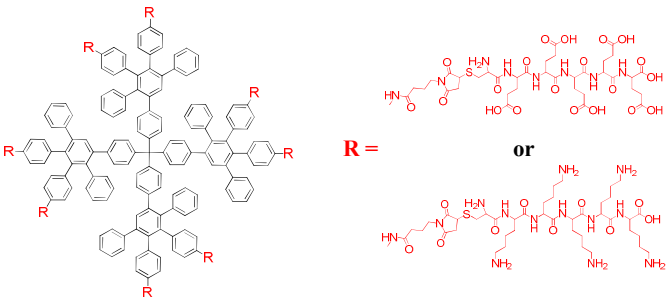

Figure 30: Peptide functionalized PPDs.

A recent breakthrough in the surface modification of PPDs came from the ability to place alternating polar (sulfonate) and unpolar (propyl) groups around the dendrimer with nano-site perfection (**Figure 31**). 1st to 3rd generation PPDs were synthesized which had between 8 (1st generation) to 32 (3rd generation) sulfonate and propyl groups on the surfaces.[131, 132] This architecture produced a non-polar dendrimer with polar patches on the periphery, where the amount, order, location, and distance of the functional groups can be determined through the synthetic modification of the organic building blocks. Moreover, the shape-persistent nature of PPDs provided

a stable nano-phase separation between the patterned polar and unpolar sections, which resulted in both attractive and repulsive forces with solvent molecules. Hence, the periphery led to a unique surface polarity for PPDs which resulted in unprecedented solubility in solvents ranging from toluene to water.

An additional aspect of the surface amphiphilicity was its impact on how the dendrimers interacted in biological applications, specifically cell uptake. Achieving efficient biological macromolecules is a significant challenge due to critical structural and conformational requirements, and there are limited examples of dendrimers that truly resemble biological species (*i. e.* proteins).[133,134] Yet with the 3D-globular nature and nano-site definition of the functional groups, combined with the lipophilic interior cavities have closed the gap between synthetic and natural amphiphiles, and made these dendrimers attractive options towards cell studies. The cavities formed by the dendrons of the PPDs match the shape and polarity of fatty acids or doxorubicin guest molecules, and nine 16-DSA ligands were accommodated indicating uptake capabilities that surpass the native protein transporter HSA. The PPD features also encouraged membrane uptake and minimized cellular toxicity, as well as the integrity of biological barriers. Thus, the refined macromolecular design emulates important features of HSA proteins and allowed trafficking payloads into A549 cancer cells and, more exciting, the permeation into endothelial cells that are a major component of the extremely tight blood brain barrier.[135] There was no significant toxicity observed after *in vivo* treatment of zebrafish embryos, compared to many reported polycations and nanoparticles. Finally, PPDs loaded with doxorubicin (an anti-tumor drug) were more efficient at transporting and releasing the molecule than HSA, indicating that it has significant potential as a macromolecular vehicle for drug delivery applications.

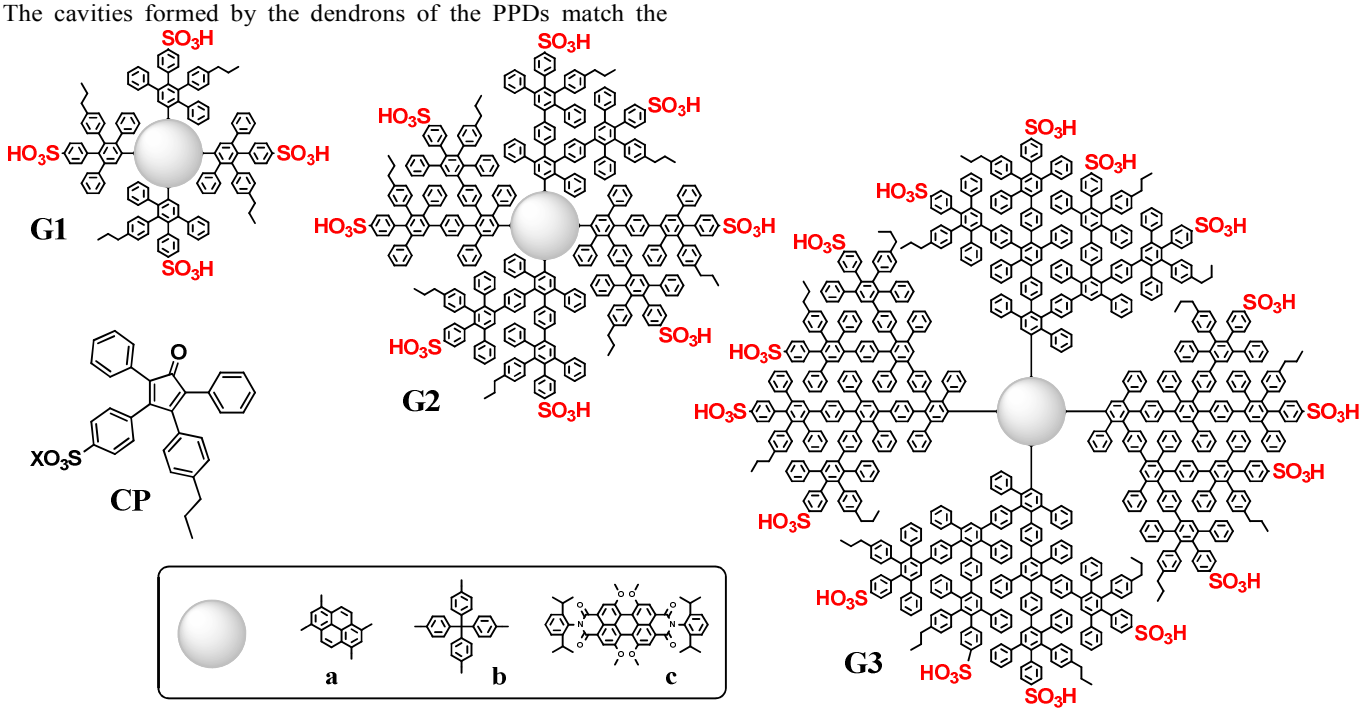

Figure 31: PPDs with "patched" surfaces of alternating sulfonate and propyl groups.

5 Conclusions and Outlook:

Polyphenylene dendrimers represent a distinct field of dendrimer chemistry based on their rigid, shape-persistent structure. They can be modified at the core, scaffold, or on the surface with various functionalities, but of significant interest is introducing different groups of varying polarity. Building PPDs around cations (phosphonium) or anionic (borate) cores leads to weakly coordinating ions that can be tuned to have different ion dissociation and conductivity characteristics. When transition metal catalysts are surrounded by bulky dendrimer arms, these dendrons shield the metal to promote stability, determine the PPD geometry, and control access to the catalytically active sites.

The polarity of dendrimer scaffolds can be tuned by the use of different moieties (*i.e.* carboxylic acids, pyridines, nitriles, thiols, nitrobenzenes, among others), to promote the uptake or encapsulation of guest molecules. These processes could be tailored by thermodynamic interactions between the guest and host species through varying the functionalities of the dendritic cavities. The stability of the dendrimer encapsulation experiments was improved by introducing azo-benzene units throughout the scaffold, which could sterically seal incoming molecules through a *trans-cis* isomerization to a "closed" configuration. Release of these molecules occurred upon the transformation back to the *trans* configuration, which represents a stimuli-responsive encapsulation and release system. Alternatively, PPDs were synthesized with thiols in their scaffolds that were used to covalently attach small molecules *via* disulfide bond formation. The bound species were discharged under reductive conditions demonstrating a reversible conjugation and release assembly.

PPD surfaces have been modified with a range of polar functionalities to encourage interactions with other materials such as small molecules, proteins, or DNA. Stimuli-responsive polymers (PS-b-PHEMA and PS-b-PAA) were synthesized by surface initiated ATRP from dendrimers, and showed versatile solubilities while also forming unique assemblies with metal oxides. Dendrimers with sulfur based ligands on their surfaces have been used to coordinate to gold nanoparticles in a procedure to form ultra-thin layer-by-layer films, while such functionalities have also been used to bridge silver interfaces for manipulating the photophysical properties of dye molecules. The asymmetric functionalization of PPDs with biotin groups was used to fluorescently tag the protein streptavidin, while other polar groups were implanted to act as sites to bind to different surfaces.

Introducing peptides or "patched" patterns of sulfonates and propyl units on dendrimer surfaces made the structures water soluble and biocompatible. The "patched" surface dendrimers demonstrate high cell uptake and low cytotoxicity, while they have even been able to cross the blood-brain barrier. These PPDs have been loaded with doxorubicin and exhibited a high efficiency of transporting and releasing the anti-tumor drug within cells.

These are some of the many accomplishments in the field of PPDs with regard to introducing various polar groups throughout the dendrimer architecture. However, by no means do we wish to limit PPDs to the past, as there is still a vast amount of potential for them in the future. Current research focuses on characterizing the crystal structure of large WCIs (phosphonium and borate) PPD ion pairs, as well as investigating their influence as counterions in metallocene chemistry. A new series of PPD based drug conjugates that possess cleavable linkers are being studied for their ability to transport and release the therapeutic drugs into cells. The field of "patched" surfaces is evolving to more intricate architectures in hopes of expanding the types of complexes that can be formed with different proteins, RNA, and DNA. PPDs are being functionalized with new peptide sequences to alter gene expression characteristics. The outlook for this genre of dendrimers looks promising, as long as the scientific imagination can continue to envision new challenges.

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synthesis and characterization of novel conjugated oligomers, polymers, dendrimers, organic high spin molecules, and hybrid spin networks.

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Klaus Müllen received his PhD in 1972 at the University of Basel in Switzerland. He was a postdoctoral fellow at ETH Zürich where he obtained his habilitation in 1977. After working as a Professor of Organic Chemistry at the Universities of Cologne and Mainz, he became the Director of the Department of Synthetic Chemistry at the Max Planck Institute for Polymer Research in Mainz (Germany) in 1989. His research interests include macromolecular and supramolecular chemistry as well as the design, synthesis, and characterization of novel organic semiconductors and graphenes for electronic and optoelectronic applications.