Development of Dendrimers: Macromolecules for Use in Organic Light-Emitting Diodes and Solar Cells

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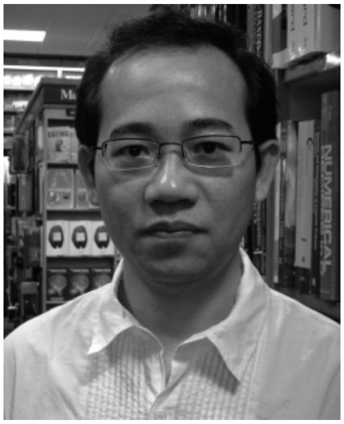
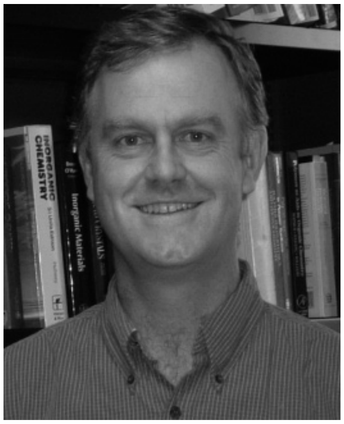
1. Introduction

Branched macromolecules or dendrimers have provided a rich seam of research in terms of both innovative chemistry and applications.[1−14] For example, dendrimers have been studied for use as low-dielectric materials,[15] as templates for the growth of single-wall carbon nanotubes,[16] as catalysts,[17−19] and in biological applications,[20−23] including biosensors,[24] magnetic resonance imaging,[25−28] and drug delivery.[29−33] However, it has only been more recently that such macromolecular structures have been explored in terms of their electronic and optoelectronic properties, which is the focus of this series of reviews. For example, charge-transporting dendrimers have become an important class of organic semiconducting material[34] and significant effort has focused on light harvesting and energy transfer from a peripheral dye or chromophore to an emissive dye at the center or focus of the dendrimer.[35−39] Organic semiconductors have become increasingly important as the active component in applications including organic light-emitting diodes (OLEDs),[40−42] transistors,[43,44] photovoltaic (PV) cells,[45,46] optical amplifiers,[47,48] and lasers.[49−51] Traditionally, organic semiconductors have fallen into two main classes, small molecules and polymers, and these materials and their applications will be covered in detail by other authors. Small molecules are generally processed by evaporation techniques and have the advantages that the structure−property relationships are relatively simple to understand, the materials are mono(disperse), and they are deposited in a pure form. On the other hand, conjugated polymers are soluble and can be deposited from solution by processes such as spin-coating and ink-jet printing, which opens up the exciting prospect of simple, fast, large-area, low-temperature device manufacturing. An additional advantage for conjugated polymers



Dr. Shih-Chun Lo carried out his chemistry studies (B.Sc. and M.Sc.) at National Chung-Hsing University in Taiwan. In 1996, he was awarded a prestigious Swire Scholarship to undertake research toward a Ph.D. at the University of Oxford under the supervision of Dr. Paul L. Burn and studied organic light-emitting diodes and solar cells using conjugated polymers. After graduating, he stayed in Oxford to carry out postdoctoral research. His recent research interests have focused on the development of dendritic organic materials for organic light-emitting diodes.



Dr. Paul L. Burn received his Ph.D. from the University of Sydney (Australia). In 1988 he moved to Cambridge University (U.K.) to carry out postdoctoral research in collaboration with Professors Friend and Holmes, and in 1989 he became the Dow Research Fellow at Christ's College, Cambridge. In 1992 he moved to a lectureship at the University of Oxford and a Tutorial Fellowship at University College, Oxford (U.K.), with an aim to develop semiconducting dendrimers. In May 2006 he was awarded a prestigious Federation Fellowship from the Australian Research Council, and from March 2007 will be Director of the new Centre for Organic Semiconductor Research at the University of Queensland (Australia).

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is that solution processing is potentially less wasteful of material than evaporation for devices that require patterning. However, it is often difficult to control the polydispersity, molecular weight, backbone defects, and end groups of conjugated polymers reproducibly. Branched macromolecules, known as dendrimers, also have the advantage of being solution processable but by careful design can incorporate the control over the optoelectronic properties that is reminiscent of small molecules. In addition, the dendritic architecture provides a number of other attractive properties, including the ability to independently control the processing and optoelectronic properties; providing the processing power to enable simple chromophores to be deposited as stable amorphous films; dendrimer generation as a tool for controlling the intermolecular interactions that govern device performance; and the ability in well-defined dendrimers to have high chemical purity. In this review, we will focus on synthetic strategies that have been investigated for the preparation of optoelectronically active solution-processable dendritic materials and concentrate on two different applications, namely OLEDs and solar cells, in which they have been used. In the context of OLEDs, we limit the discussion to light emission, as branched macromolecules for charge transport will be discussed in the review by Shirota. We will also briefly comment on other recent light-emitting and -absorbing branched molecular materials that have been used in OLEDs and solar cells.

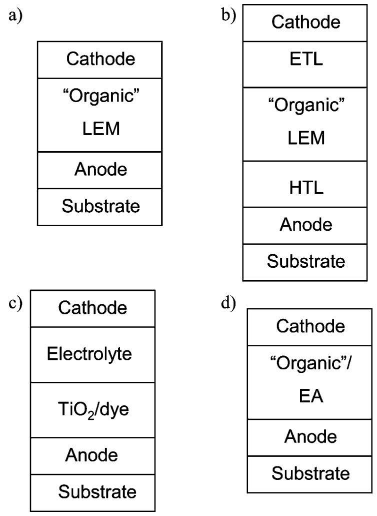


Figure 1. Device structures illustrating: (a) a simple single-layer organic light-emitting diode (OLED) containing an organic light-emitting material (LEM); (b) a multilayer OLED with hole transport (HTL) and electron transport (ETL) layers designed to balance charge injection and transport [For each type of OLED, the LEM may be either a neat film or a guest/host blend, with the latter being especially important for simple phosphorescent molecules.]; (c) a dye-sensitized (Grätzel) photovoltaic cell; (d) a bulk heterojunction solar cell where the organic material is blended with an electron acceptor (EA).

2. Organic Light-Emitting Diodes and Photovoltaic Cells

Before reviewing the design strategies and types of dendritic materials that have been developed for OLEDs and PV cells, it is instructive to have a brief discussion of the requirements that these applications place on the materials. The simplest OLED has the emissive layer sandwiched between two electrodes (Figure 1a).[41] At the cathode, electrons are injected into the lowest unoccupied molecular orbital (LUMO), and at the anode, holes are injected into the highest occupied molecular orbital (HOMO). The two charges move through the layer under the applied bias, and if they meet on the same (macro)molecule, they can form an exciton which may decay to give out light with the color of the emitted light governed by the HOMO−LUMO energy gap of the material. To have an efficient OLED, it is necessary to have balanced charge injection (equal numbers of holes and electrons) and transport, capture of all the injected charges to form excitons, and radiative decay of all the excitons. This has not yet been achieved in OLEDs comprised of a single material, and hence, more complex devices are usually prepared (Figure 1b).[52,53] Consequently, in order to balance hole and electron injection and transport, one or more extra layers are usually incorporated between the light-emitting layer and the cathode and/or the anode. For example, if the light-emitting layer transports holes predominantly, then at least one electron-transporting layer will be placed between the emissive layer and the cathode and *vice versa*. In the process of injecting charge (holes or electrons), it is not possible to control the spins of the electrons, and hence, when they meet on the same (macro)-molecule, there is a certain probability that they form a singlet or triplet exciton. For small molecules, the ratio of singlets to triplets is 1:3,[54] while, for conjugated polymers, the ratio of singlets to triplets is believed to be greater, although triplets are still formed.[55] If the material is fluorescent, then only the singlets can emit light, while if it is phosphorescent, both the singlets and triplets can be captured for light emission. Therefore, phosphorescent materials inherently have the potential to form the most efficient devices. While this has been demonstrated for red and green emitters,[52,53] phosphorescent deep blue emitters are still a significant challenge. In a neat light-emitting layer, the chromophore that is responsible for light emission is generally also responsible for charge transport. This often leads to a trade-off between these two important properties. For good charge transport, close interactions of the chromophores are required. However, for light emission, interactions of the chromophores can lead to emission from aggregates or excimers. Excimer formation leads to a change of emission color and a reduction in the photoluminescence quantum yield (PLQY). Therefore, the ability to engineer the intermolecular interactions at a molecular level is critical. For small molecule phosphorescent emitters, the intermolecular interactions are controlled by blending the emitter in a host.[54,55] As will be highlighted in this review, dendrimers are proving to be ideal materials for controlling these interactions at the molecular level for solution processed light-emitting materials. It is also important that the emissive chromophore has a high solid-state PLQY; that is, once the exciton is formed, it must decay, emitting a photon before being quenched by nonradiative processes within the device. Finally, it should be noted that not all light generated escapes out the front of the device, with a significant proportion, of order 80%, being wave-guided out of its edges. The best devices have internal quantum efficiencies approaching 100%; that is, for every injected electron, a photon is generated, and this corresponds to an external quantum efficiency of 20% based on a fifth of the light generated coming out the front of the device.

Photovoltaic cells act in the opposite way to OLEDs in that light is absorbed, the formed exciton is separated, and then the separated charges have to migrate to the electrodes

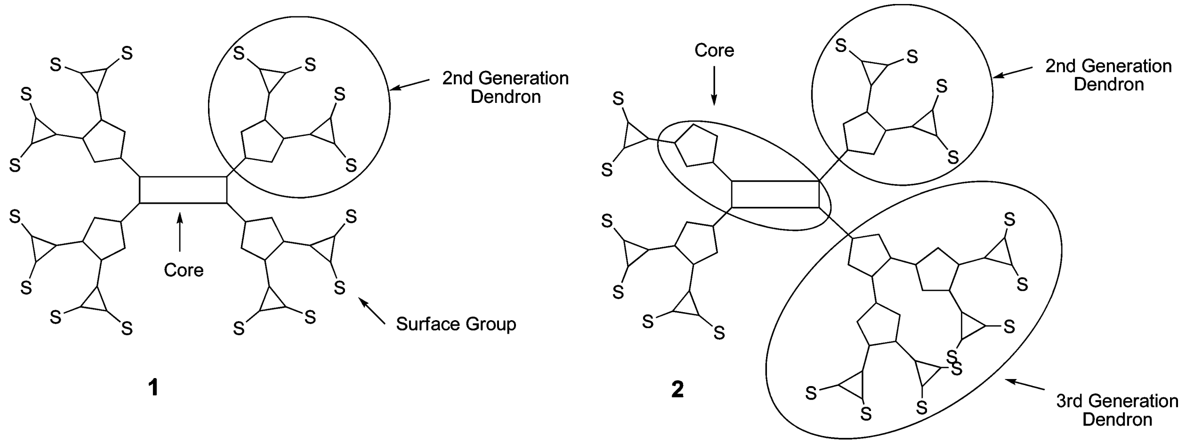


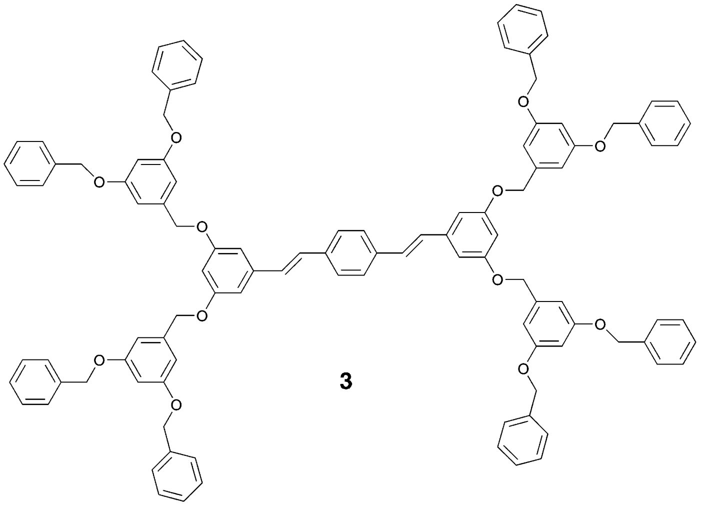
Figure 2. The well-defined dendrimer **1** has four dendrons (branching groups) attached to the rectangular core. The dendrimer is a second-generation dendrimer with one level of each of pentagon and triangle branching points. Such a dendrimer would be typically formed from a convergent route. Dendrimer **2** has randomness within its branching with different generations of branching within its structure. In both cases, S = surface groups.

without being quenched. The ideal material must have a high absorption coefficient and be able to absorb light with wavelengths that correspond to the solar spectrum. The exciton, formed on absorption of a photon of light, is relatively strongly bound, and hence, simple neat single layer devices tend to be very inefficient. As a consequence, more complex device structures are generally used, of which the dye sensitized (Grätzel) cell (Figure 1c)[56] and bulk heterojunction cells (Figure 1d) are the two most successful types.[57,58] These two cell classes provide a large interface between materials of different electron affinities. In the Grätzel cell, a dye is absorbed onto an inorganic semiconductor such as titanium dioxide. On excitation, the electron from the exciton formed on the dye is transferred to the inorganic semiconductor and then hops to the electrode and travels around the circuit. The oxidized dye is then reduced via an electrolyte ready for another excitation. In a bulk heterojunction cell, instead of having the “layered” device structure, the materials with different electron and hole affinities are blended. When an exciton is formed on the hole-transporting material (low electron affinity), the excited electron hops onto the high electron affinity material. The two charges then have to move through the layer by hopping between regions of their respective materials to the electrodes. The main materials used as electron acceptors in bulk heterojunction PV cells are fullerene derivatives, for example [6,6]-phenyl-C_{61}-butyric methyl ester (PCBM). In both cell types, high charge mobility is required, but unlike the case of OLEDs, there is not a tradeoff between charge transport and purity of light emission and so materials can be optimized for the former property. Nevertheless, it is important to note that the efficiency of a cell is dependent on how well the absorption and solar spectra are matched. The best power conversion efficiencies (η) reported for bulk heterojunction cells and Grätzel cells are now over 5%[58] for the former and around 11% for the latter.[59] It is important to note that comparison of efficiencies of PV cells is somewhat difficult due to the different reporting methods. For example, some results are only reported for single wavelengths while others are at low incident light intensities. For ease of comparison, the overall power conversion efficiency (η) should be quoted for devices of similar size under air mass 1.5 global intensity (AM1.5) conditions, which simulate the solar spectrum and have an incident light power of 100 mW/cm^2.[59]

3. Dendrimer Structure and Synthetic Strategy

Dendritic materials are branched macromolecules that can be divided into two main classes: (1) those that have well-defined structures and are characterized by a polydispersity of one (**1** in Figure 2) and (2) those that have structures where there is randomness within the branching (**2** in Figure 2), which often leads to larger dispersity in the molecular weight. In both cases, several key units—the core, the dendrons that contain branching points between which one or more linking groups may be found, and, optionally, surface groups—define the structures. In random highly branched materials, it might be difficult to elucidate the position of the core although it can be defined as the unit that provides the first level of branching. The electroactive or optoelectronic moieties in a dendritic structure may be found at the core of the macromolecule or within the branching and/or linking groups or at their distal ends. The position of the active chromophores will be governed by the desired application. For example, light-emitting dendrimers that are used in OLEDs generally have their emissive chromophore at the core of the structure. Dendrimers are defined by the number of different levels of branching, that is, the generation number, and while this is easily determined for structures of type **1** in Figure 2, it is less easily done for the type **2** structures.

The two main synthetic strategies applied to the formation of dendrimers are the convergent[60,61] and divergent routes.[62−67] In a convergent synthesis the dendrimer is built from the surface or outside inward. The advantages of the convergent route are well-known and include the following: the number of reactions at each iteration to form a higher generation is limited to the number of active functional groups on each branching point; the surface groups can be included early in the synthesis and hence can impart solubility throughout the dendrimer synthesis; and purification is more straightforward, as a missing branch will impart a larger difference on the size and polarity of the dendrimer. This procedure gives rise to a structure that is precisely defined, is monodisperse, is of high purity, and is without ill-defined end groups. One criticism that has been made of the convergent route is that



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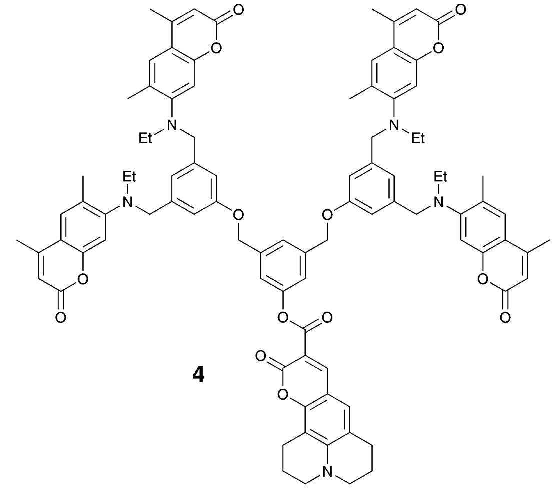

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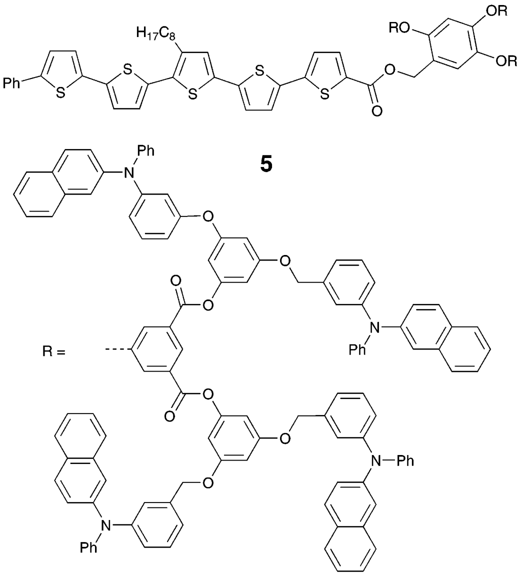

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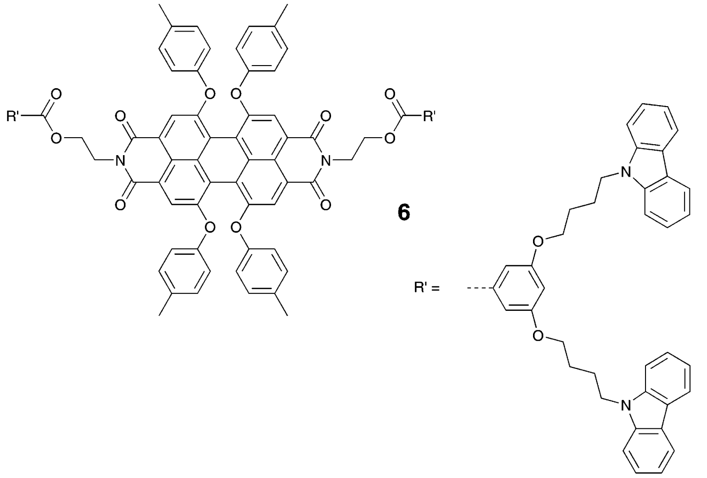

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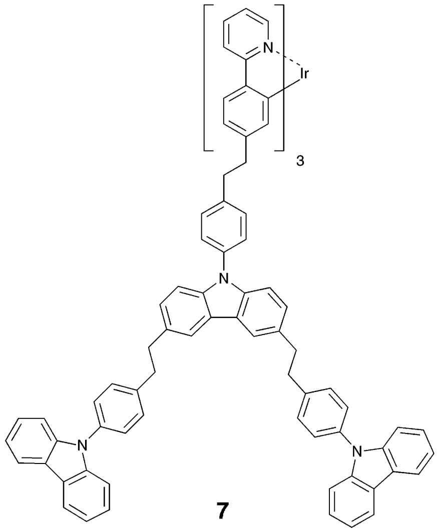

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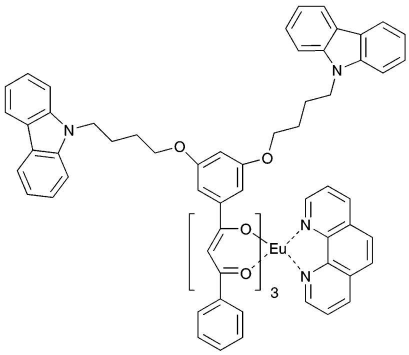

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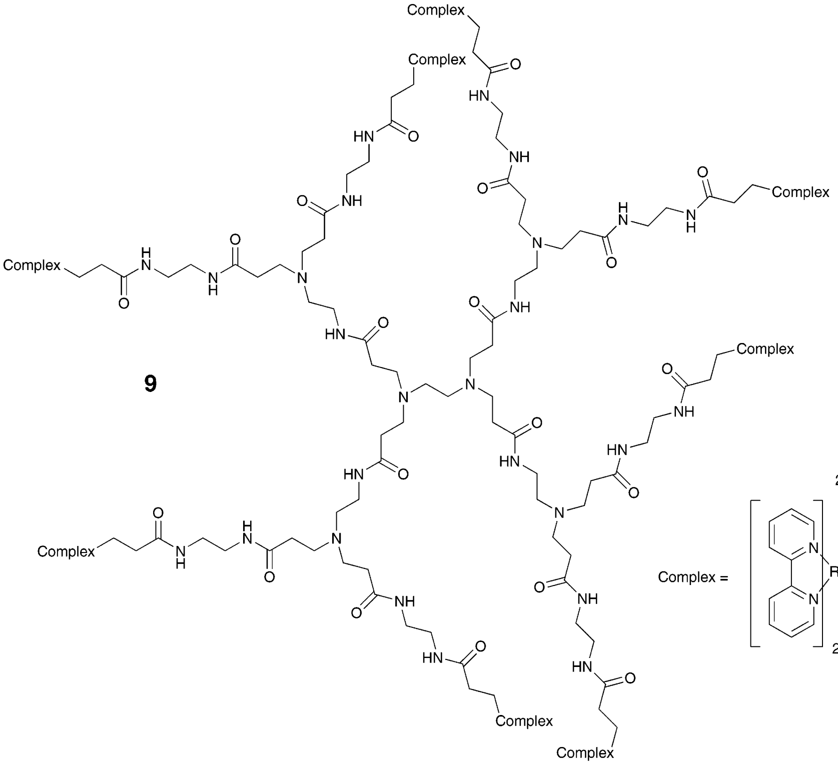

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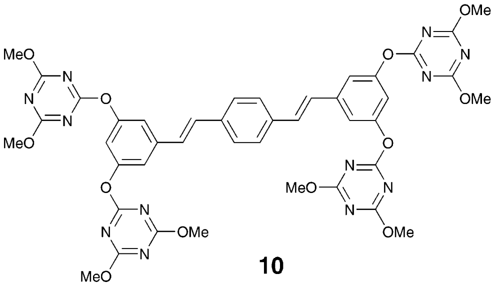

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Figure 3. Light-emitting dendrimers with "charge-transporting" moieties at their surfaces (**4**−**8**) and a light-emitting chromophore at the core (**3**−**8** and **10**). Dendrimer **10** has triazinyl branching groups in the dendrons.

it gives rise to slow growth. This is true, and if high generations were needed, then the convergent route creates a problem. However, for dendrimers to be of commercial use in optoelectronic applications, the development of high generations is not needed, with the functionality being incorporated into low-generation materials. In contrast, the divergent route builds the dendrimer from the inside out. In terms of optoelectronic materials, the divergent route has three distinct disadvantages. First, as the generation number increases, the number of "individual" reactions also increases, meaning that there can often be unreacted functional groups or end groups (in polymer terminology). Given that the control of end groups is vitally important in conjugated polymer performance, the introduction of a potentially large number of end groups is of critical concern for dendritic materials. This can be obviated to a certain extent if only low-generation materials are prepared. Nevertheless, the purity and polydispersity of the dendrimers prepared via the divergent route will be more difficult to control than those prepared via the convergent process. To avoid as many unreacted end groups, it is necessary to use reactions that are very high yielding. This immediately places a limit on the number of different reaction types that can be used, and ultimately on the range of useful dendritic materials that can be made. Finally, the functionality of the surface group plays a critical role in the processing of the dendrimers. An optoelectronic dendrimer often requires that its structure has a significant number of conjugated units, which generally have low solubility in the absence of solubilizing groups. Solubilizing groups have the most effect on the surface of the dendrimer, and hence, introducing them late in the synthesis will create difficulties during the reaction and purification of the intermediate stages. An advantage of the divergent route is that if there is complementary functionality on different branching points, then it is very easy to form very large structures, sometimes termed "hyperbranched" polymers. However, these dendritic materials are structurally poorly defined, they are polydisperse, and the issue of end groups becomes critical.

In order to provide some structure to the discussion, the review will divided into the main functionality that is found in the branching framework or dendrons and the dendrimers will be discussed under two different general headings, namely saturated and conjugated branched structures. For the sake of clarity, different dendrimer types will be illustrated with low-generation structures although in many cases higher generation materials have also been developed.

4. Saturated Dendrons

There are many studies on dendrimers that are comprised of electronic chromophores but have saturated (nonconjugated) linkages.[68] The main types of linkages used have involved benzyl ethers (Fréchet), esters, amines, or amides. While there are many studies on the photophysical properties of the materials, there are fewer instances where such materials have been incorporated into devices. Three general structural types have been developed for light-emitting dendrimers for use in OLEDs. The first structural type of dendrimer has had electrically insulating flexible dendrons, with the chromophore that is responsible for light emission and charge transport buried in the center (**3** in Figure 3).[69−72] The dendrimers were generally prepared using a convergent route. For example, in the case of **3**, the Fréchet dendrons were synthesized first with the final step being formation of the dendrimer by the reaction of a 1,4-phenylenedimethylene diphosphonate with an aldehyde focused Fréchet dendron. The devices based on the dendrimer were not very efficient, and this is in part due to the saturated dendrons. Evidence for the potentially detrimental effects of having simple saturated dendrons attached to an emissive core comes from a study of dendrimers based on structures similar to **3** but having differing numbers of dendrons. For single layer devices (ITO/dendrimer:PVK/Al) [ITO = indium tin oxide; PVK = poly(vinylcarbazole); Al = aluminium] with the different dendrimers blended at the same molar concentration in PVK, the device containing the dendrimer with only one dendron attached to the emissive core had higher current densities than that with two dendrons. In addition, the device containing the higher generation dendrimer generally had lower efficiencies.[73] That is, the greater the amount of insulating material, the poorer the performance. This study on the effect of the number of dendrons attached to the emissive core raises an important point about dendrimer structures that is further illustrated by the dendrimers in Figure 3. Dendrimers **4** and **5** have only one dendron attached to the core whereas dendrimers **3** and **6** have two. As will be seen later, the number of dendrons attached to a light-emitting chromophore can play an important role in controlling the important interactions that govern device performance.

The second approach to light-emitting dendrimers with saturated dendrons also has the emissive chromophores at the core of the dendrimer. However, charge-transporting moieties are introduced at the surface of the dendrimer[74] in an effort to overcome the poor charge transport (for example **4**,[75] **5**,[76] and **6**[77] in Figure 3). The dendrimers contain ester and ether linkages and were prepared via convergent routes with the emissive chromophore added at the focus of the dendrimer in the final step. The initial OLEDs containing these dendrimers as the light-emitting layer showed only modest performance in simple device structures. For example, devices containing dendrimer **5** were reported to have external quantum efficiencies of 0.12% at undefined brightness in the red region.[76] More recently, the strategy of having charge-transporting groups at the surface of the dendrimer has been further elaborated with high-generation dendrimers (up to generation five) being synthesized with coumarin 343 or pentathiophene dyes at the core.[78] In the case of the latter, the dendrons were attached to both ends of the chromophore. An important feature of these materials is that by encapsulating the cores in the higher generation dendrimers, it is possible to tune the color of emission by blending the coumarin 343 and pentathiophene cored dendrimers in different ratios, as the higher energy excitons formed on the coumarin 343 cored dendrimer are not completely transferred to the lower energy red emissive pentathiophene chromophore due to site isolation. The devices again showed modest performance with the best results for a three-layer device (ITO/PEDOT:PSS/dendrimer:PBD/BCP/Alq$_3$/LiF/Al) [PEDOT:PSS = poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate); PBD = 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole; BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenathroline; Alq$_3$ = tris-(9-hydroxyquinolate)aluminum(III); LiF = lithium fluoride], which had the fifth-generation thiophene cored dendrimer blended with an electron-transporting material (PBD) and electron transport layers (BCP and Alq$_3$) to assist in balancing charge injection and transport. The device had a maximum external efficiency (EQE) of 0.76% and a power efficiency of 0.59 lm/W at a brightness of 100 cd/m^2. The incorporation of dendrimers with charge-transporting moieties at their surfaces has also been studied in the context of phosphorescent emitters. Phosphorescent emitters have the advantage in that both the singlets and triplets formed in the device can be captured, leading to more efficient OLEDs. For example, a *fac*-tris(2-phenylpyridyl)iridium(III) cored dendrimer with dendrons comprised of carbazole moieties linked by ethylene units has been prepared (**7** in Figure 3). The device structure investigated was (ITO/PEDOT:PSS/**7**/Ca/Al) [Ca = calcium], with the emissive layer being comprised of neat dendrimer or a blend with PBD. The devices containing the neat dendrimer films had much broader emission spectra than the blended films, indicating strong intermolecular interactions of the emissive cores in the solid state. However, very good device performance (EQE = 7.6% at around 5 V and a brightness of 20 cd/m^2) was achieved when the dendrimers were blended with the electron-transporting PBD.[79] Europium(III) complexes with carbazole moieties at the surface of the dendrons have also been reported (for example **8** in Figure 3).[80,81] Interestingly, instead of observing the red emission normally associated with the f−f transitions of the europium(III) complexes, the emission was white due to there being more than one emissive species: the europium itself and excimer or exciplex emission caused by interaction of the carbazole surface groups and the carbazole-containing host material.[80]

The final structural type has the emissive chromophore at the surface of the dendrimer. If the chromophore is also the charge-transporting moiety, then this structure type has the potential advantage of good charge transport, as the chromophores should be close together. However, this has to be traded off against potential concentration quenching of the luminescent chromophores. These effects have been studied with a series of poly(amidoamine) (PAMAM) dendrimers with ruthenium complexes at their surfaces (for example **9** in Figure 3). While there was little change in the solution PLQY between dendrimer generations, it was found that, in the solid-state, moving from the first- to the third-generation dendrimer, the charge mobility decreased due to the large proportion of insulating material, and the EQE of the devices (ITO/dendrimer/Au) [Au = gold] at a given voltage decreased by a factor of 2 to 0.05%. This decrease in device efficiency is most probably due to self-quenching of the chromophores in the solid state.[82]

For all dendrimers, the branching groups play an important role, and in terms of aromatic branching groups, the phenyl

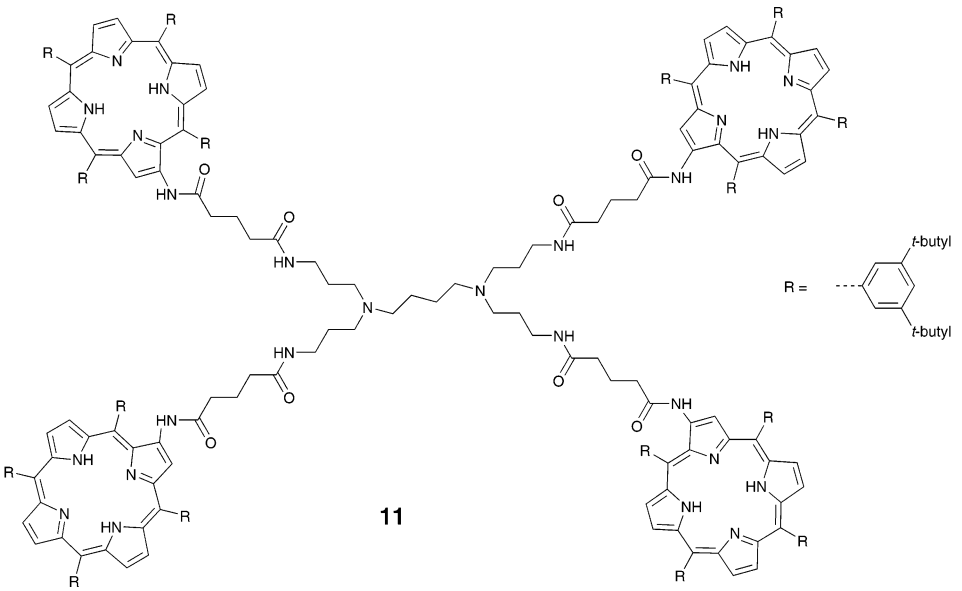

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Figure 4. First-generation propylene imine-based dendrimer **11** with four porphyrins at its periphery. The solubility of the dendrimer is imparted by the 3,5-di-*tert*-butylphenyl groups on the *meso* positions of the porphyrin rings.

ring is most commonly used. Two other aromatic branching groups have been investigated with saturated dendrons. Triazine moieties at first sight are an excellent choice for branching groups.[83,84] 1,3,5-Trichlorotriazine is a commonly used reagent, and each of the chlorine groups can be substituted sequentially with nucleophiles such as oxygen, nitrogen, and sulfur. The substitution of each chlorine atom with one of the nucleophiles deactivates the next chlorine atom toward substitution, and hence, the branching group can be chemoselectively substituted with three different groups. The first example of using this strategy for light-emitting dendrimers was in the preparation of **10** (Figure 3). **10** was formed by a convergent route where the two methoxy groups were added first to the 1,3,5-triazine trichloride with the final chlorine atom of 2 equiv of the dimethoxychlorotriazine derivative being substituted by the more stable phenoxy anions of 3,5-dihydroxybenzaldehyde. Using the more stable anion in the final substitution meant that the methoxy groups were not displaced.[85] The synthesis of distyrylbenzene chromophore was completed by the coupling of 2 equiv of the aldehyde focused dendrons with tetramethyl-1,4-phenylenedimethylene diphosphonate. Films of **10** were reasonably luminescent with a film PLQY of 31%, although the devices were not particularly efficient.[85] This and more recent work has suggested that some triazine-based dendrimers do not have suitable stability for optoelectronic devices and, hence, while attractive from a synthetic point of view, may be impractical from a device standpoint.[56] More recent work on dendrimers with pyrimidine branching units has shown that they can also be easily synthesized and have better stability than the corresponding triazine branched dendrimers.[87] Triazole moieties have also been used as branching groups in aryl ether- or amine-based dendrons, although the photophysical and device properties of materials containing these branching points have not yet been studied.[88,89]

The study of dendrimers containing saturated dendrons in PV devices is still very much in its infancy. There have been a number of reports of saturated dendrimers containing porphyrins.[90−93] One set of reports describes a family of materials based on propylene imine dendrimers with porphyrins at their periphery (**11** in Figure 4).[92,93] The dendrimers were prepared by a divergent route with the 2-aminoporphyrins coupled onto the surface groups of the preformed dendrimer using a diamide linking unit. The coupling was efficient enough for the formation of a third-generation dendrimer that had 16 porphyrin rings added to the surface; that is, all the surface groups reacted. The porphyrin−propylene imine dendrimer showed enhanced absorptivity when compared with that of nondendritic porphyrin reference material. Bulk heterojuction cells were prepared where the porphyrin−propylene imine dendrimers were blended with C_{60} and the incident photon to photocurrent conversion efficiency (IPCE) values of the devices containing the low-generation porphyrin-capped dendrimers were found to be higher than those of the devices comprised of the simple porphyrin. Interestingly, the efficiency of the devices using the higher generation dendrimers was less than those of the lower generation ones and the simple porphyrin. This was attributed to poorer $\pi-\pi$ interactions of the C_{60} with the porphyrin rings in the high-generation dendrimer matrix due to steric crowding. In a Grätzel-like cell using nanostructured tin oxide, a maximum IPCE value of 15% was observed for the blend containing the low-generation dendrimer **11**, and an overall power conversion efficiency (η) of 0.32% with a visible light input power of 6.2 mW/cm^2 was reported. Finally, a Grätzel-type cell with fullerene units spaced by first-generation amido amine (PAMAM) dendrimers has also been described. It was found that the IPCE and η of the cell increased logarithmically with the number of fullerene layers with the η for the device with three fullerene layers being 0.13% at an incident light power of 42.5 mW/cm^2.[94]

5. Conjugated Dendrons

5.1. Arylacetylenes

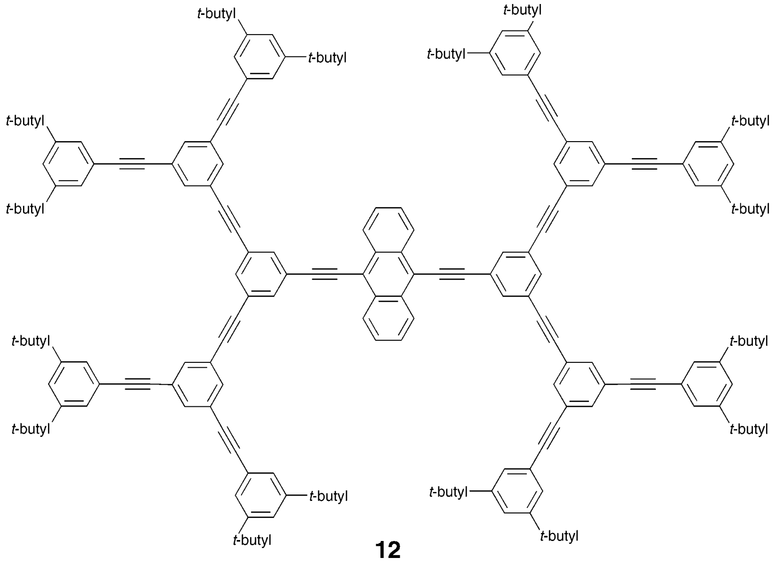
The main arylacetylene structural unit investigated for dendrimers is that based on phenylacetylene. Elegant syntheses of phenylacetylene-based dendrimers (phenyl branching points and acetylene linkers) have been widely reported. In spite of the structural variations, the main method used for their preparation is based on Sonogashira chemistry[95−97] and a convergent strategy. The main reason for the use of the convergent route is that it allows the introduction of surface groups at the beginning of the synthesis that provides solubility to what are otherwise poorly soluble conjugated materials. It is important to note that the conjugated and linear nature of the phenylacetylene moiety means at low generations the dendrimers can adopt a relatively planar form in the solid state. However, high generation dendrimers cannot adopt a planar arrangement in the solid state due to steric interactions.[98] One of the main emphases of the work on phenylacetylene-based dendrimers has been to develop materials for the study of energy transfer. This is where the dendrimer is excited primarily at a chromophore at the surface of the dendrimer and the energy is then transferred to a chromophore with a smaller HOMO−LUMO energy gap at the core. Dendrimers have been prepared that have been comprised only of the diphenylacetylene moieties, that is with a single acetylene unit between each phenyl branching point of the dendrimer (**12** in Figure 5) or several phenylacetylene units between the branching phenyls. If the attachment of the three acetylene units is *meta* around the branching phenyl, then although the dendrimers are fully conjugated, the electrons are not fully delocalized. This gives rise to a similar effect to that observed for the dendrimers with saturated linkers whereby the macromolecular dendritic structure is comprised of individual chromophores. If two of the acetylene units are *para* to each other on the branching phenyl unit, then this gives rise to extended conjugation within the branching component of the dendrimer (**13** in Figure 5).[99,100] It is important to note that the modular nature of dendrimer synthesis allows great creativity and flexibility in structure; that is, different components can be incorporated into the same dendron structure to form “asymmetric dendrimers”. For example, dendrimer **14** (Figure 5) contains both benzyl ether (Fréchet) and diphenylacetylene units and is prepared using a mixture of Williamson ether synthesis and Suzuki and Sonagashira reactions.[101]

However, in spite of the extensive synthesis and photophysical studies on dendrimers containing acetylene units, there have been few reports of their use in optoelectronic devices. The first reported OLEDs with a light-emitting dendrimer layer contained materials with structures based on **12** (Figure 5) with diphenylacetylene moieties in the dendrons and a 9,10-di(phenylethynyl)anthracene core.[102] Although the OLEDs emitted light, the emission was broad, indicative of excimer emission, and no efficiency data was reported, suggesting that they did not work particularly well. The excimer emission arises from the planarity of the phenylacetylene-containing dendrimers allowing the emissive chromophores to interact strongly in the solid state. The incorporation of hole-transport diphenylamine groups in place of the *tert*-butyl groups on the surface of the dendrimer[102] or the inclusion of the electron-transporting oxadiazole units[103] did not significantly improve the efficiency of the devices. For example, an OLED (ITO/PEDOT:PSS/**15**/Al−Li alloy) [Li = lithium] comprised of **15** (Figure 5) with the electron-transporting oxadiazole units and the same emissive 9,10-di(phenylethynyl)anthracene core as **12** had an external quantum efficiency of 0.02% at an unspecified brightness. At this time there have been no reports of solar cells that contain dendrimers with acetylene units as the main linking units within the structure.

5.2. Arylalkenes

Arylalkene-based dendrimers have been one of the most widely studied families of dendrimers with *trans*-stilbenyl (*E*-stilbenyl) moieties within the branching framework playing a major role in the structures. The conjugated nature of the *E*-stilbenyl moieties has also meant that surface groups are required to facilitate purification and processing of the materials. Like the phenylacetylene-based dendrons and dendrimers at low generation (first and second), the *E*-stilbenyl dendrons are mostly planar, and it is not until the third generation that steric interactions cause a more significant distortion from planarity. Most of the dendrimers containing the *E*-stilbenyl-based dendrons have had the optoelectronically active component at the core of the dendrimer,[104] although there have been a few reports where the active moiety is at their surface.[105−107] The problem with this latter approach for luminescent materials is that chromophores are able to interact easily, leading to quenching of luminescence. There are two main convergent strategies reported for forming *E*-stilbenyl-based dendrimers: first, the components can be connected by forming the double bond using Wittig-type chemistry[108,109] and, second, the vinyl unit can be added directly to the next aryl unit using palladium-catalyzed chemistry.[110−113] Both these processes have been successfully utilized in convergent syntheses. Recently, an alternative approach to stilbenyl dendrons has been reported in which the basic dendron framework is built up with sulfur linkages and then oxidation of the sulfides to sulfones followed by a series of Ramburg−Backlund reactions is used to introduce the vinylene moieties late in the synthesis.[114] While this method successfully gave first- and second-generation dendrimers, it could not be used to form higher generation materials. This was due to the fact that the reagents in the Ramburg−Backlund reaction could not reach the reactive sites buried in the larger structures. To make optoelectronic dendrimers, the normal route has been to make the dendrons first and then use functionality at the foci of the dendrons to form the dendrimer. This method gives rise to reproducible syntheses of mono(disperse) materials. Examples of dendron syntheses leaving reactive functionality at the foci of the dendrons are illustrated in Scheme 1. Dendron **16** (Scheme 1) has been prepared by coupling bisphosphonate **17** with aldehyde **18** in a Wittig−Horner reaction. Deprotection of the acetal at the foci of **16** to leave an aldehyde then allows an iterative buildup of higher generation dendrons or reactions to form a core.[108] An alternative approach to similar dendrons with aldehydes at their focus has been achieved using Heck methodology. In this case a styrene, for example **19** (Scheme 1), is reacted with 3,5-dibromobenzaldehyde (**20**) to give the dendron **21** with an aldehyde at its focus.[110] This can then be converted to a vinyl unit to allow the iterative procedure to occur and higher generations to be formed. A similar strategy has been utilized but replacing the 3,5-dibromobenzaldehyde with 3,5-diiodoaniline with the amine moiety subsequently elaborated to allow for further coupling reactions.[115] An elegant variation on the synthesis of such dendrons utilizes sequential Heck and Wittig−Horner reactions with the advantage of this latter procedure being that high-generation dendrons are prepared in a small number of steps.[116]

In terms of dendrimers with the optoelectronic component at the center, as stated earlier, the functionality at the foci of the dendrons plays an important role, as it provides the means of creating the core chromophore. For example, the



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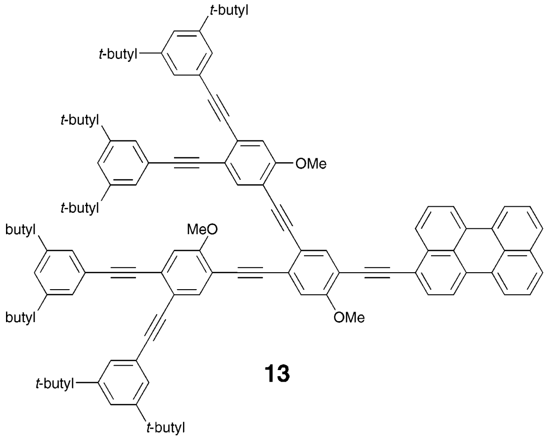

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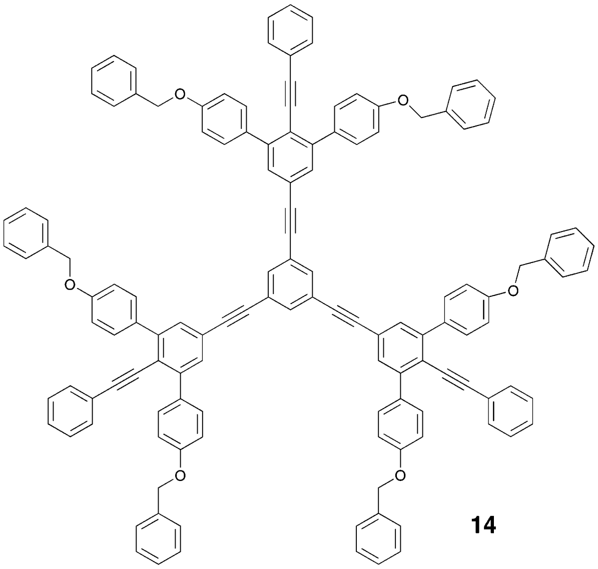

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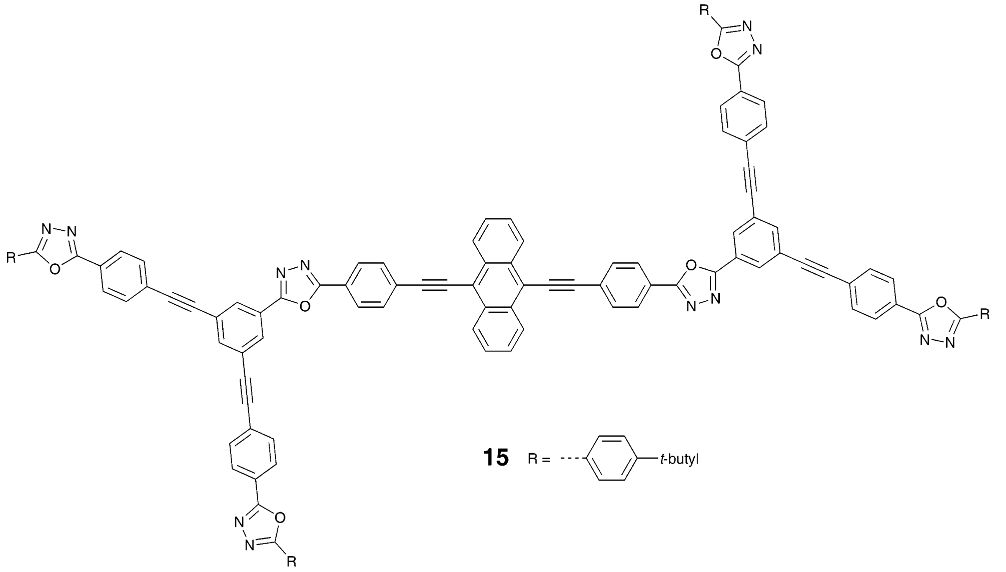

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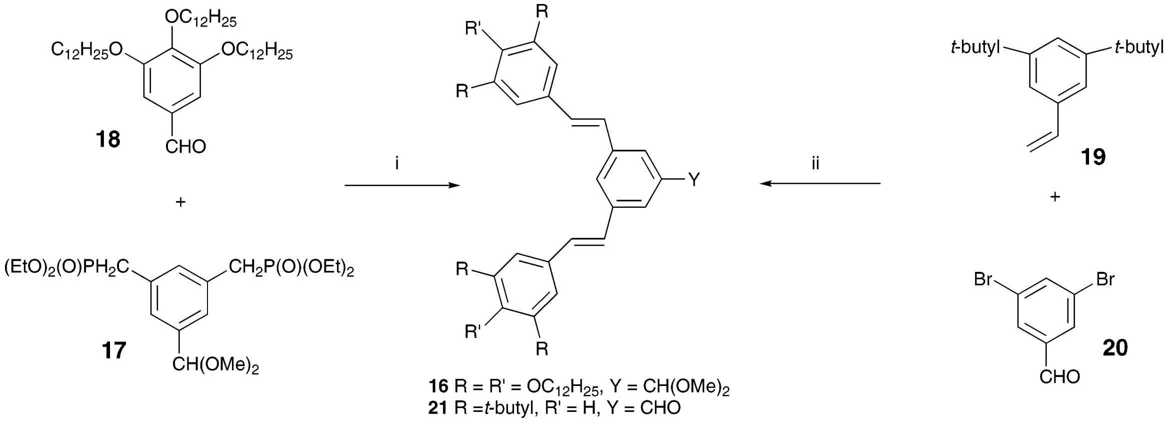
Figure 5. Acetylene-containing dendrimers with *meta* (**12**) and *para* (**13**) arrangements around the phenyl branching groups, an "asymmetric" dendrimer with benzyl ether and acetylene components (**14**), and a dendrimer containing oxadiazole electron-transporting moieties (**15**).

Scheme 1. Examples of Wittig−Horner and Heck Approaches to *E*-Stibenyl Dendrons with Reactive Functionality at Their Foci[a]



16 R = R' = $OC_{12}H_{25}$, Y = $CH(OMe)_2$
21 R = *t*-butyl, R' = H, Y = CHO

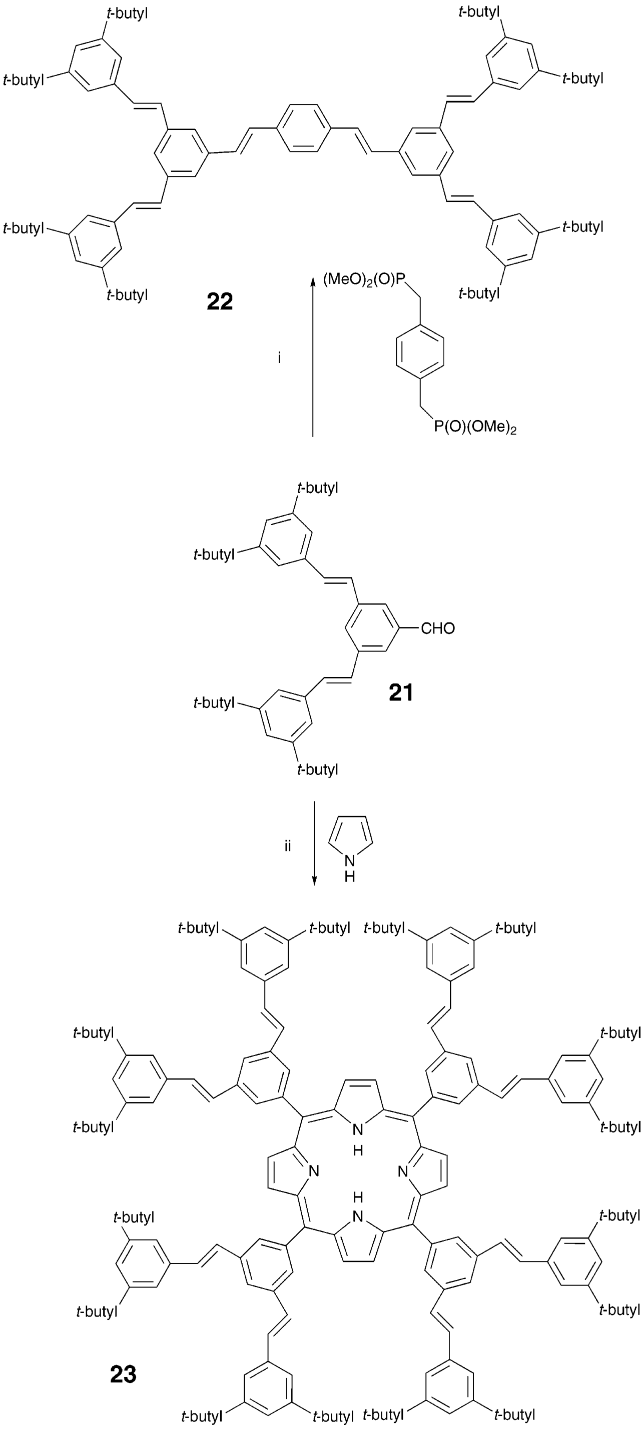
[a] (i) Potassium *t*-butoxide, tetrahydrofuran;[108] (ii) *trans*-di(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II), 2,6-di-*tert*-butylcresol, anhydrous *N,N*-dimethylacetamide, Ar, ≈130 °C.[110]

aldehyde moiety at the focus of **21** has been used to form light-emitting dendrimers with chromophores that emit different color light. This is illustrated by the reaction of **21** with tetramethyl-1,4-phenylenedimethylene diphosphonate that gave a blue emissive distyrylbenzene chromophore at the center of dendrimer **22** (Scheme 2) while condensation with pyrrole gave red emissive dendrimer **23** (Scheme 2) with a porphyrin core.[110]

For application in OLEDs, dendrimers with *E*-stilbenyl dendrons and fluorescent emissive cores have been used to illustrate many of the key light-emitting dendrimer properties. The first property illustrated is the ability to independently control the processing and emissive properties. For example, while **22** and **23** emit blue and red light, respectively, they can both be processed under the same conditions to give good quality thin films. Second, while there are many chromophores that are fluorescent in solution, they cannot generally be processed to form amorphous thin films and their luminescence is often quenched in the solid state. For example, distyrylbenzene itself cannot be spin-coated to form good quality amorphous films and *it is the dendritic architecture of **22** that provides the processing power*. That is, the use of dendrimers opens up a wider range of chromophores that can be used in devices. Third, dendrimer generation is a powerful tool for controlling the intermolecular interactions that govern OLED performance. In OLEDs, there is often a trade-off between charge transport and light emission. For good charge transport, the chromophores need to be close together so the hopping distance is short. However, if the charge-transporting chromophores are also responsible for emitting light, then close proximity can lead to aggregate formation and excimer emission. By using dendrimer generation, these key interactions can be controlled at the molecular level. The effect of generation was first studied on three generations of dendrimers with distyrylbenzene chromphores (**22** is the first generation in the series).[117] For this family of dendrimers, it was found that the device efficiency was greater for the higher generations than for the first generation. It was also found that while the emission spectrum of the first generation was quite broad due to excimer emission, the spectra of the higher generations narrowed as the dendrons protected the emissive chromophore of the dendrimers and reduced the intermolecular interactions that lead to excimer emission. The improvement in the device performance could have been due to a decrease in nonradiative decay pathways and/or more balanced charge injection and transport. To elucidate a more precise reason for the improved device performance four generations of dendrimers with the same dendrons as **22** but with fluorescent tris(distyrylbenzene)amine chromophores (**24** in Figure 6) were prepared.[118] In these latter dendrimers, it was found that charge was directly injected into the tris(distyrylbenzene)amine chromophores at the center of the dendrimers and that the mobility of the injected holes decreased by a factor of 100 in going from the “zeroth-” to third-generation dendrimer.[119,120] That is, as the hopping distance between the chromophores increased with generation, the mobility of the holes decreased. The change in mobility was accompanied by a concomitant increase in the light-emitting device efficiency, providing the first direct evidence that generation could control charge mobility and give improved device performance given that the film PLQYs of the materials were similar.[118] Finally, the *E*-stilbenyl dendronized dendrimers were used to illustrate the importance of the connectivity of the components. While the dendrons of **22**, **23**, and **24** are fully conjugated, the electrons are not fully delocalized due to the *meta* arrangement around the branching phenyl rings, similar to the *meta* arranged phenylacetylene-based dendrons. This strategy of “connectivity” has also been utilized with the emissive chromophores. For example, the dendrimers with tris(distyrylbenzene)amine chromophores have the orbital density distributed across the three distyrylbenzenylamine “chromophores”[121] but the equivalent tris(distyrylbenzene)benzene cored dendrimer (**25** in Figure 6) has each of the distyrylbenzenylbenzene moieties as individual chromophores because of the *meta* arrangement around the central phenyl ring.[122]

As with the optoelectronic dendrimers with saturated dendrons, the common branching group used for the arylalkene dendrimers has been the phenyl ring. However, there has been one report of a branched macromolecule that has a single triazine moiety as the branching unit at its center with three phenylenevinylene chromophores extending from it and long liphophilic alkoxy chains to give it solubility.[123] In addition, nitrogen (**26** in Figure 6)[124] and carbon atoms (**27** in Figure 6)[125] and triazines (although the triazines are substituted by three aryl units, **28** in Figure 6)[126] have also been used as branching moieties with arylalkene dendrimers. It is interesting to note that the dimensionality of **27** will be different from that of **22** due to there being three substituents around the vinyl moiety. This arrangement means that the dendrons cannot be planar at low generations unlike the

Scheme 2. Examples Showing How the Functionality at the Focus of the Dendron Can Be Used To Create Blue (22) and Red (23) Emissive Chromophores at the Center of a Dendrimer[a]



[a] (i) Potassium *tert*-butoxide, anhydrous tetrahydrofuran, rt, N$_2$ followed by iodine, toluene, Δ; (ii) dry dichloromethane, catalytic trifluoroacetic acid, rt, followed by 2,3-dichloro-5,6-dicyano-1,4-quinone.[110]

dendrimers containing the *E*-stilbenyl units. While many of the dendrimers are formed via convergent routes, one interesting divergent synthesis of dendrimers with carbon branching units constructed with alternating vinylene and acteylene units utilizes a combination of Wittig and Sonagashira reactions. The synthetic strategy requires the coupling of two *p*-formylacetylenes with a 1,1-dibromo-2-phenylalkene using a Sonogashira reaction. The aldehydes are then reacted with triphenylphosphine and carbon tetrabromide in the next iterative step to introduce the 1,1-dibromovinylene unit ready for the next Sonagashira reaction.[127]

The triazine units in dendrimers such as **28** (Figure 6) were designed to improve electron transport, although two-layer devices (ITO/PVK/dendrimer/Al:Li) only had modest EQEs in the range $\approx$0.03−0.5%. Finally, in terms of light-emitting dendrimers with arylalkene dendrons, the first phosphorescent dendrimer OLED contained a platinum-chelated porphyrin core and *E*-stilbenyl dendrons; that is, **23** chelated with platinum(II). The device was not very efficient, as the *E*-stilbene dendrons were found to quench the phosphorescence.[128]

All the syntheses discussed thus far have given rise to mono(disperse) materials. A number of highly branched arylalkene-based materials have also been investigated. There are two main strategies for making highly branched materials. The first is to have two or more monomer units, one of which must have at least three functional groups that can react with the two or more functional groups on the other monomer(s). The second method is to have the complementary reactive groups on the same monomer. The reactions are often defined by the number and/or type of reactive groups on each of the momoners. For example, an A*x*B*y*-type reaction can be used to describe a monomer unit that contains *x* functional groups of type A and *y* functional groups of type B. Alternatively, and somewhat confusingly, the notation can also be used to describe a reaction that involves monomers of type A and B, which have *x* and *y* reactive groups, respectively. The simplest arylalkene structure is **29** (Figure 7), which is only comprised of phenyl and vinylene units.[129] **29** was prepared by Heck reaction of 1-bromo-3,5-divinylbenzene (an AB$_2$-type monomer) in yields of up to 50% and an $\bar{M}_w$ of 9000. However, unlike the convergent route to well-defined dendrimers that have a polydispersity of one, the polydispersity of **29** was 2.7 and the material had reactive surface groups. Surprisingly, even in the absence of lipophilic solubilizing groups, the material had sufficient solubility for solution processing. The solubility of **29** is in contrast to that of linear poly(1,4-phenylenevinylene), which is completely insoluble in common solvents. The solubility of **29** is probably due to the branched nature of the material causing twists in the structure and hence making it more difficult to $\pi-\pi$ stack in the solid state. Although the materials showed good solution PLQYs, they have not yet been incorporated into device structures. A similar branched phenylenevinylene material has been synthesized via Wittig reaction of the AB$_2$ unit, 3,5-diformylbenzyltriphenylphosphonium bromide.[130] This second strategy has further been elaborated to produce materials with alkoxy substituents on the inner phenyl ring[131,132] and pyridyl or dimethylaminophenyl groups at the end of the branches. The latter materials have been used in OLED structures, which have had, at best, modest performance.[133,134] A complex highly branched arylenevinylene structure has also been formed by the Heck reaction of **30** and **31** (Figure 7). The material thus formed had the relatively high $\bar{M}_w$ of 6.0×10^4 and the low polydispersity of 1.1 and had good solubility, with the latter attributed to the lipophilic alkoxy groups. Bilayer devices (ITO/dendrimer/Alq$_3$/Al) had a luminous efficiency of around 0.33 cd/A at a brightness of 500 cd/m^2 and 6.3 V.

There has been very little work on dendritic materials with arylalkene units for photovoltaic devices thus far. One

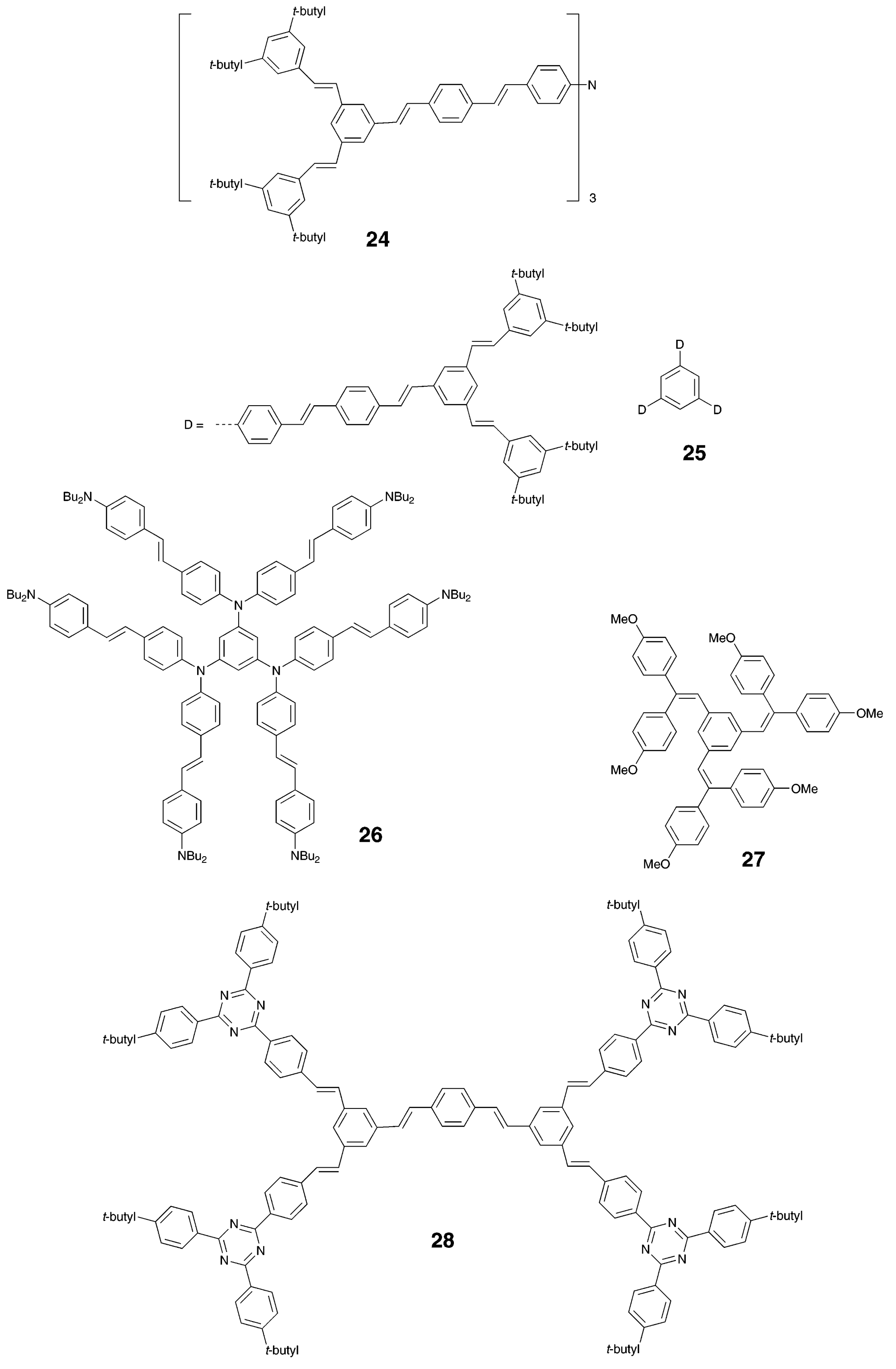


Figure 6. Amine- and phenyl-centered dendrimers, and phenyl, amine, and triazine branching groups.

material that has been synthesized has had *meta*-linked dendrons comprised of stilbene units with dialkyamine surface groups (for example **32** in Figure 7) or alkoxynapthyl chromophores at the distal ends of the dendrons covalently attached to C_{60}. Although charge separation of the exciton was shown to occur upon excitation, a necessary step in PV cell operation, no device performance was reported.[135]

5.3. (Hetero)arylenes

The final main class of dendrimers used in opto-electronic applications are those in which the branched components are comprised of (hetero)aryl−(hetero)aryl connectivity. In terms of OLED applications, these materials have proved to be the most successful and give highly efficient devices. Unlike arylacetylene- and arylalkene-based dendrons that tend to be planar at low generations, one of the key advantages of the (hetero)arylene−(hetero)arylene dendrons is that they form a more nonplanar geometry even at low generations due to the steric interactions of the substituents *ortho* to the (hetero)arylene−(hetero)arylene bond. The fact that the dendrons are nonplanar even at low generations means that control over the intermolecular interactions of

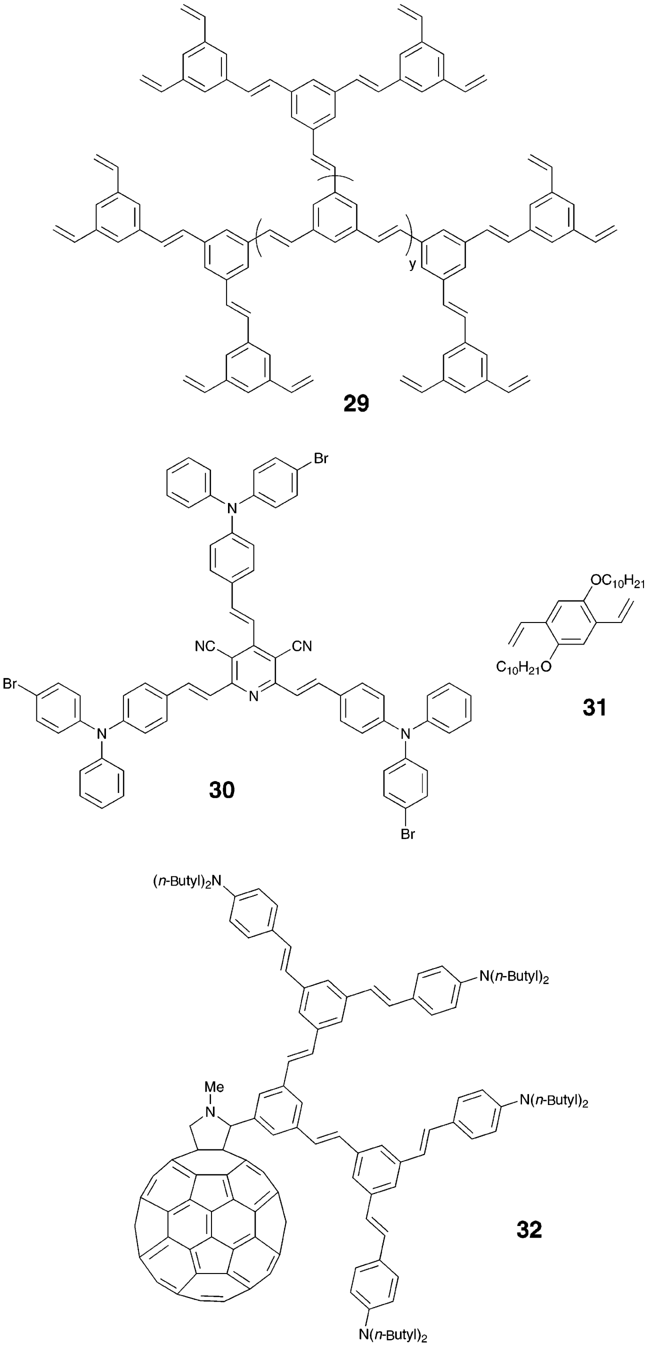
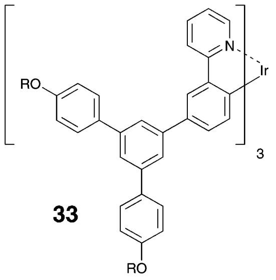


Figure 7. Highly branched phenylenevinylene structure (**29**) and starting materials (**30** and **31**) that can be used to form such materials. A dendronized C_{60} (**32**).

the chromophores at the centers of the dendrimers is greater even for lower generation dendrimers. Many of the (hetero)arylene−(hetero)arylene materials are prepared by palladium catalysis methods, and a number of these will be illustrated. The main family of dendritic materials comprised of (hetero)arylene−(hetero)arylene components have the dendrons made of phenyl units connected to each other, and these can be further subdivided into Müllen-type dendrons with four or five phenyl rings and those with three phenyl units[136−138] around the branching phenyl ring. The synthesis of Müllen-type dendrimers has been widely reported and reviewed, although, in the context of their use in optoelectronic applications, there have been far fewer reports. The most successful light-emitting dendrimers for OLED applications have had iridium(III) complexes as the cores, to which three or more phenylene-based dendrons are attached.[139,140] The dendrimers are prepared via a convergent route whereby the dendrons are first synthesized and then attached to the ligand, which is subsequently complexed to the iridium(III) metal.[141] For example, the phosphorescent green emissive dendrimer **33** (Figure 8) was prepared in a convergent manner, in which the first step was the attachment of the solubilizing 2-ethylhexyl groups to *p*-bromophenol. A series of metalation and boronate ester formation and Suzuki couplings gave the dendronized 2-phenylpyridyl ligand in good overall yield before complexation with the iridium(III).[141] By changing the ligand structure but keeping the same dendrons, it is also possible to achieve phosphorescent dendrimers with red[142,143] and sky-blue emission.[144] These phosphorescent dendrimers gave rise to highly efficient OLEDs due to their ability to capture both the singlets and triplets that are formed in the devices as well as controlling the intermolecular interactions that govern charge transport and light emission. In addition, the *meta* linking of the phenyl units meant that the triplet energy of the dendrons was sufficiently high to avoid quenching of the phosphorescent cores. For example, the green emissive dendrimer **33** when blended in a host and used in a bilayer device achieved a brightness of 400 cd/m^2 at 4.5 V, with a corresponding EQE of 16% and a power efficiency of 40 lm/W.[145] This is very close to the theoretical limit of efficiency of 20% based on an outcoupling of a fifth of the light generated in the device. More recently, highly efficient two-layer devices with a neat dendrimer emissive layer and an electron-transport layer have also been reported whereby the attachment of a dendron to both (hetero)aryl components of the ligand (**34**, Figure 8) encapsulated the charge-transporting and emissive core.[140] This latter device (Figure 8) is the simplest and most efficient OLED containing a solution-processed light-emitting layer.

Müllen-type dendrons[146] as a component of phosphorescent dendrimers have been less widely investigated. Dendrimers with Müllen-type dendrons are of interest for controlling the important intermolecular interactions, as they are more highly branched than those used for **33** and **34**. The strategy used for the synthesis of such dendrimers is a combination of the Diels−Alder chemistry developed by Müllen and that used for the preparation of **33**. That is, an acetylated 2-phenylpyridyl ligand is reacted with 2,3,4,5-tetraphenylcyclopentadienone and then the dendronized ligand is complexed to the iridium(III). The first light-emitting phosphorescent dendrimers, for example **35**, with Müllen dendrons suffered from poor solubility due to the lack of surface groups.[147] More recently, this has been overcome by the attachment of surface groups to dendrons, leading to very efficient devices (EQE > 10%) when the dendrimers were blended with 4,4′-bis(*N*-carbazolyl)biphenyl (CBP).[148]

Fluorescent dendrimers with both the simple phenylene dendrons used for **33**, for example **36** and **37**,[149] and Müllen dendrons have also been reported. An important feature in the syntheses of **36** and **37** is that the same dendron type used for the preparation of **33** and **34** could also be used in their preparation. That is, the boronic acid or boronate ester focused dendrons were reacted with 2-(3-bromophenyl)pyridine to give the ligand for **33** and were reacted with bis-2,2′-(7-bromo-9,9-di-*n*-hexylfluorene) and 2-(5-bromothiophenyl)-7-bromofluorene to give **36** and **37**, respectively. This demonstrates the advantage of the modular nature of dendrimer construction. That is, it is possible to have libraries of dendrons and cores with different combinations of



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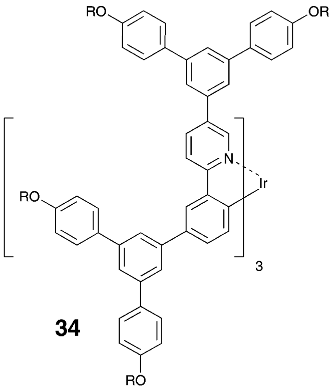

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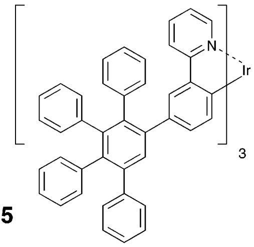

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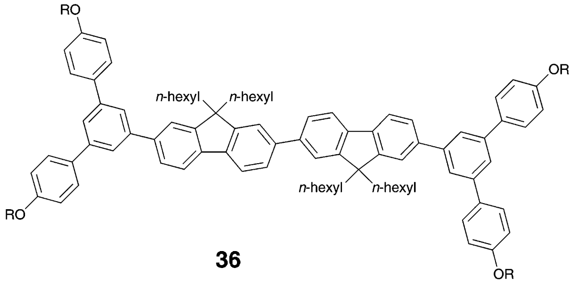

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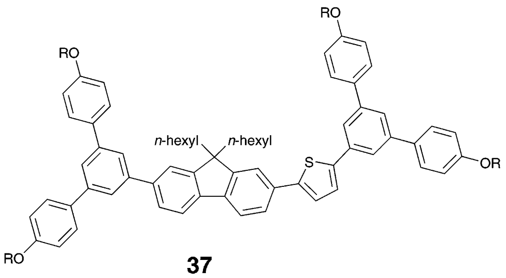

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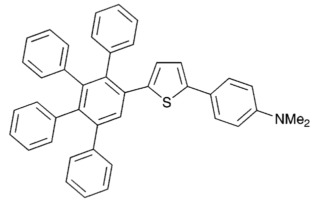

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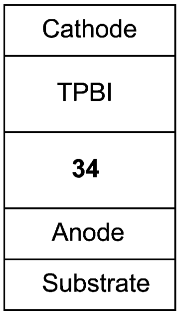
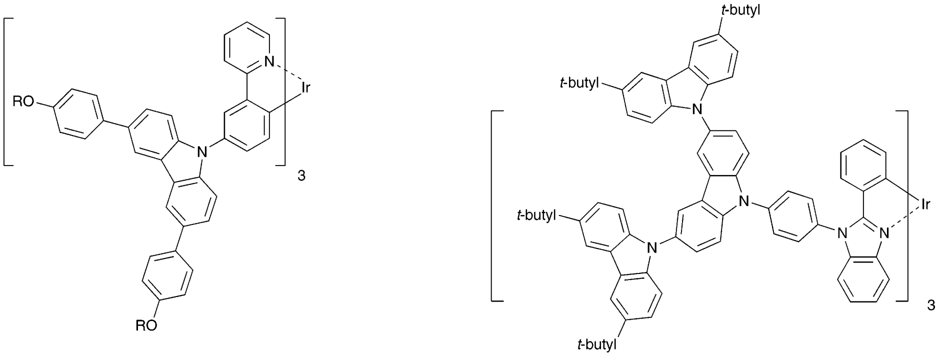


Figure 8. Phosphorescent (**33**−**35**) and fluorescent (**36**−**38**) dendrimers with phenyl-based dendrons, and the structure of the efficient two-layer OLED containing a neat film of **34** and a 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) electron-transporting layer. R = 2-ethylhexyl.

components being drawn from the libraries to give rapid access to new dendrimers. Interestingly, **36**, with the bis-fluorenyl core, emits a deep blue fluorescence while the fluorenyl−thiophenyl-cored dendrimer **37** gives a blue-white emission. The emission of **36** is deeper blue than normally required for displays, but as **36** and **37** have the same dendrons and surface groups, they can easily be blended. An important feature of the devices that contained blends of the two materials was that as the ratio of the two light-emitting components changed, the color of the emitted light varied between the two limits of the devices containing the neat materials.[149,150] Fluorescent dendrimers with simple phenlyene dendrons without surface groups have also been used in OLEDs. For example, two first-generation phenylene dendrons, similar to **33** but without the 2-ethylhexyloxy surface groups, were attached to the 9 and 10 positions of anthracene.[151] The lack of surface groups also meant that the dendrimers needed be blended with PVK to allow processing, and devices with an electron-transporting moiety in the blend gave good performance for a blue emissive material, with maximum external quantum and luminous efficiencies of 1.5% and 1.5 cd/A, respectively. Dendrimer **38** (Figure 8) is an example of a first-generation Müllen dendronized blue fluorescent emitter. The best fluorescent device containing **38** (ITO/PEDOT:PSS/PVK:**38**/BCP/LiF/Al) as the emissive material had an external quantum efficiency of 1.6%. The need for PVK as a host again probably arose from the fact that the materials were not very soluble, due to the lack of surface groups, similar to the case of **35**.[152] High-generation Müllen dendronized dendrimers



39 **40**

Figure 9. Carbazole-containing phosphorescent dendrimers. R = 2-ethylhexyl.

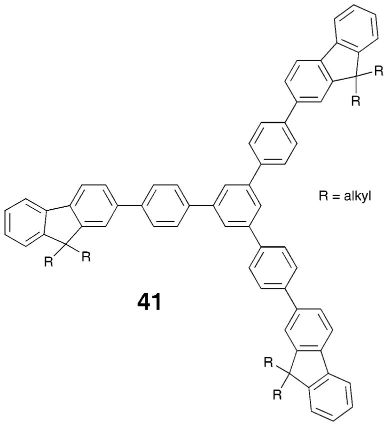
with perylenetetracarboxidiimide cores have also been reported.[153] Alkyl surface groups were attached to make the dendrimers solution processable. Single-layered OLEDs gave reddish orange emission with low efficiency (0.14 cd/A). Interestingly, the turn-on voltage (when light is observed) of the OLEDs was found to be dependent on the generation, with the higher generation having the higher turn-on voltage. This is due to the fact that the phenylene dendrons are electrically insulating and the higher generations are shielding the electroactive core and slowing charge injection and transport.

A final method for forming phenyl branching groups that has only been explored a little is based on condensation chemistry. For example, acetophenone can be condensed with Lewis acid catalysis to give 1,3,5-triphenylbenzene. This type of chemistry has been used to prepare the core precursor for **25**[154] and, more recently, truxene-based dendrimers in excellent yield, although OLEDs based on these latter dendrimers were not very efficient (EQE = 0.16%).[155]

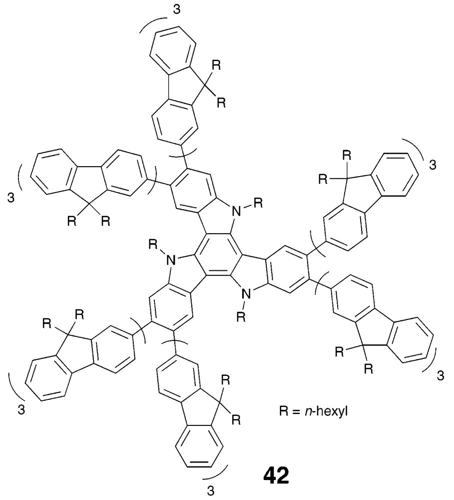
An interesting development in (hetero)arylene-based dendrons has been driven by the use of phosphorescent emitters in OLEDs. The most efficient OLEDs based on small molecular phosphorescent emitters all have the emitter blended in a host matrix with a majority of the hosts containing carbazole units, for example, CBP and TCTA [TCTA = 4,4′,4″-tris(*N*-carbazolyl)triphenylamine].[54,55,145] The host can play a role both in charge transport and in preventing quenching of the luminescence caused by aggregation of the emissive species. The dendritic architecture can achieve the same role of the host in terms of controlling intermolecular interactions, and hence, it was logical to develop dendrons comprised of carbazole units and attach them to the phosphorescent core. As seen earlier in the review, there are examples of this strategy whereby the carbazoles are anchored and connected via nonconjugated ethylene linkages.[79] A couple of iridium(III) complex-cored dendrimers with conjugated carbazole-containing dendrons have also been reported (**39** and **40** in Figure 9).[156,157] One of the key results of changing the phenyl-based dendrons to carbazole dendrons, for example, moving from **33** to **39**, was that the hole mobility was found to be enhanced for the latter. The explanation for this was reported to be that the HOMO orbital density is distributed more onto the dendron in the case of **39** compared to **33**, making it simpler for the charge to hop from one dendrimer and/or dendron to next.[156] Bilayer devices (ITO/PEDOT:PSS/**40**/TPBI/LiF/Al) [TPBI = 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene] containing a neat emissive dendrimer film of **40** showed good performance with an external quantum efficiency of 8.8% at 100 cd/m^2 and 3.5 V.[157] Carbazole dendrons have also been attached to porphyrin[158] and ruthenium complex cores,[159] although they have not been used in optoelectronic devices as yet.

There have been a large number of reports of well-defined branched macromolecules with (hetero)arylene chromophores that contain just a single branching atom or group at the center of the material. For example, silicon[160] and nitrogen atoms[161,162] and silsesquioxane,[163] phenyls,[164,165] truxenes,[155,166] triazatruxenes,[167,168] triazines,[169] and porphyrins[170,171] have been used. While the chemistry for the attachment of the chromophores to the center of the material varies, the chromophores themselves are generally synthesized by various metal-catalyzed reactions. Although the photophysical properties of many of the materials have been studied, few attempts have been made to incorporate them into device structures. One bilayer OLED (ITO/NPD/**41**/Ca) [NPD = 4,4′-bis(*N*-{1-napthyl}-*N*-phenylamino)biphenyl] containing **41** (Figure 10), prepared by vacuum deposition, gave blue emission with an EQE of 1.2% at 10 V.[172] In a second example, single-layer devices (ITO/PEDOT:PSS/**42**/Ba/Al) [Ba = barium] containing spin-coated triazatruxene **42** (Figure 10) gave good blue emissive devices with Commission Internationale d'Eclairge (C.I.E.) 1931 color coordinates of (0.15, 0.09) and a maximum EQE and luminous efficiency of 2.0% and 2.1 cd/A, respectively, at a brightness of 602 cd/m^2 (29 mA/cm^2 and 11.7 V).[168] Finally, (hetero)arylene-based dendrimers with a central branching point and organometallic complexes (platinum and ruthenium) at the surface have been prepared, although the OLEDs have tended to be relatively inefficient.[173,174]

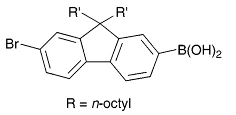
All the (hetero)arylene-based materials described thus far have been well-defined materials with a polydispersity of one. As with the arylalkene moiety, highly branched arylene-based dendrimers have also been synthesized using palladium- or nickel-catalyzed cross-coupling reactions.[175−177] For example, a one-pot Suzuki coupling of **43** and **44** (Figure 11) led to highly branched materials with $\bar{M}_w$'s in the range of 4−12 × 10^4.[176] As with a majority of these types of syntheses, the materials formed tend to have larger polydispersities than those prepared via a convergent methodology. For example, materials prepared from an $A_2A'_2B_3$ combination of monomers (where A_2 and A'_2 are dibromo and diboronate ester fluorenyl derivatives, respectively, and B_3 is a tribromooxadiazole derivative) utilizing palladium-catalyzed Suzuki coupling reactions have been reported to have polydispersities of 2.4−2.6 and $\bar{M}_w$'s of 3.7−4.7 × 10^4.[178] Importantly, in both studies, it was recognized that the materials suffered from the presence of a large number of reactive end groups. These were reacted with complementary reagents in the final steps of the syntheses in an attempt to fully cap the end groups with unreactive func-



41



42



43

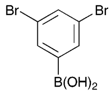


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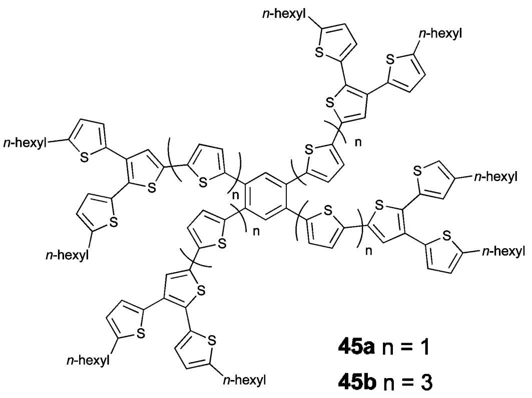
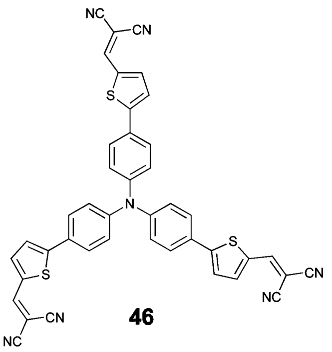
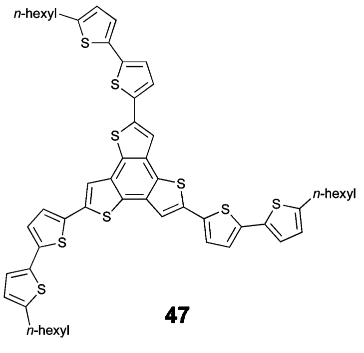
Figure 10. Materials with single branching units at the center (**41** and **42**) and starting materials to form highly branched arylene-based dendrimers (**43** and **44**).



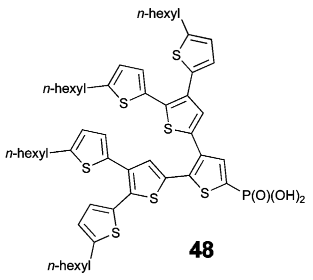
45a n = 1
45b n = 3



46



47



48

Figure 11. Thiophene-containing dendritic materials and dendron.

tionality.[176,178] The best OLEDs based on the highly branched materials were reported to have a maximum EQE of 2.5% (ITO/PEDOT:PSS/dendrimer/Ca) although the brightnesses were not reported.[179]

Thiophene has a smaller HOMO−LUMO energy band gap than benzene, and oligothiophenes can have good charge transport due to efficient packing in the solid state. Therefore, dendritic thiophenes have been recently investigated for photovoltaic applications. Both well-defined (for example **45a**,**b** in Figure 11)[180] and highly branched[181] materials have been synthesized with the former utilizing Stille reactions and the latter utilizing nickel-catalyzed couplings for their formation. For the dendrimers based on **45**, it is important to note that the extended thiophene units of **45b** ($n = 3$) offered better overlap of the absorption with the solar spectrum and enhanced hole mobility. A power conversion efficiency (η) of 1.3% at AM1.5 has been reported for a PV cell containing **45b** blended with PCBM (ITO/**45b**:PCBM/Al).[182] A number of well-defined branched macromolecules with triphenylamine or tris(thieno)benzene cores and thiophene-containing arms have also been reported and used in PV cells. For example, bilayer PV cells with **46** (formed

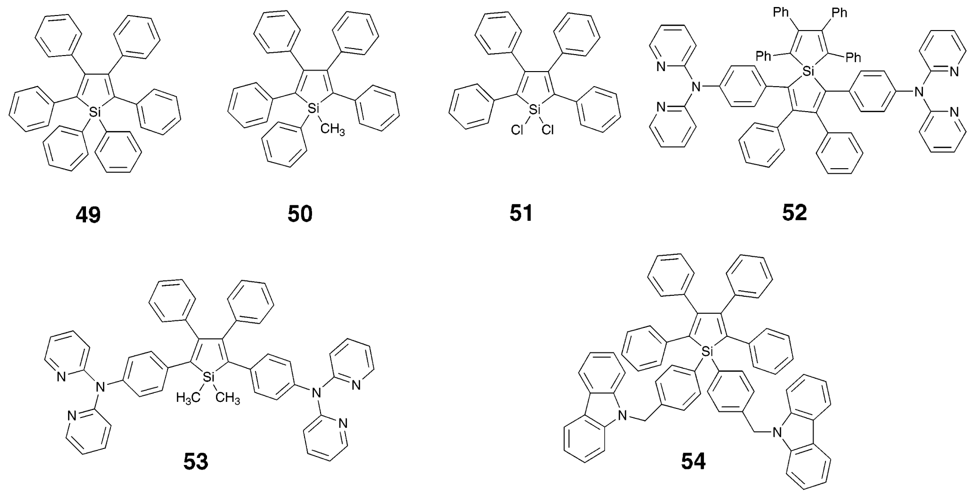


Figure 12. Silole-based materials.

in a divergent manner using Stille, Vilsmeier−Haack, and condensation reactions) had a maximum power conversion efficiency (η) of 1.0% at AM1.5 in a bilayer device (ITO/**46**/C_{60}/Al).[183] A similar material but with perylene moieties at the distal ends when blended with PCBM had an η of 0.25% in a nonoptimized device (ITO/PEDOT:PSS/dendrimer:PCBM/Al).[184] A good performance, $\eta = 1.3\%$, was reported for the branched thiophene **47** in a heterojunction solar cell with a perylene electron-accepting layer (ITO/PEDOT:PSS/**47**/perylene/LiF/Al), although this was at low incident light intensity (1.9 mW/cm^2).[185] The enhanced performance was attributed to improved light absorbance, horizontal orientation of the materials to the electrode surface, and increased π-electron delocalization. Nevertheless, these results are still significantly below those of the best oligo and poly(thiophene) PV devices. An interesting photovoltaic material has thiophene-based dendrons (for example **48** in Figure 11) with a phosphonic acid at its focus complexed to CdSe nanocrystals.[186] Single-layer photovoltaic cells (ITO/**48**:CdSe/Al) showed initial power conversion efficiencies of 0.29% at an illumination intensity of 0.14 mW/cm^2.

6. Siloles

An interesting class of branched molecules are those based on the silacyclopentadiene moiety. Simple examples of this type of material are **49** and **50** (Figure 12), and they are notable due to the fact that their photoluminescence is increased in the solid state and they have electron-transporting characteristics due to the lowered LUMO. The solution photoluminescence quantum yields of **49** and **50** were 30% and 13%, respectively, while the film PLQYs were significantly higher at 78% and 85%, respectively. The improvement on luminescence in the solid is opposite to that normally seen for emissive chromophores, where the emission decreases in the solid state, and this difference has been attributed to the emission coming from an aggregate.[187] Devices incorporating **50** have been reported to have external quantum efficiencies ranging from 0.65%[188] to up to 8% (20 cd/A) (ITO/CuPc/TPD/**50**/Alq_3/Al) [CuPc = copper phthalocyanine; TPD = 4,4′-bis(*N*-3-methylphenyl-*N*-phenyl)biphenyl].[189,190] An external quantum efficiency of 8% for a singlet emitter with a small molecule chromophore is more than would normally be expected. **50** has a film photoluminescence quantum yield of 85%, and taking into account the standard singlet to triplet ratio of 1:3 and an out-coupling of light of 20%, the maximum external quantum efficiency should be 4.5%. The higher efficiency observed is not fully understood but could come from the fact that emission arises from an aggregate, which perhaps changes the ratio of singlet to triplet formation or gives a much greater out-coupling of the light. Further evidence for the importance of the aggregation for light emission from these materials comes from studies of highly branched silole-containing materials. In the highly branched materials, which pack less well in the solid state, there was no aggregate-enhanced emission.[191] The branched silacyclopentadienes and their structural variants are relatively easily made, and the syntheses often include acetylene-based substrates.[192,193] For example, when diphenylacetylene is treated with lithium and then silicon tetrachloride, the dichlorosilacyclopentadiene (**51** in Figure 12) is formed. The two chlorine atoms can be easily substituted to give different derivatives. For example, reaction of **51** with 2 equiv of the phenylacetylide anion gave the diphenylacetylene derivative, which was cyclized with lithium naphthalide with the subsequent dianion trapped as the bis-zinc salt of a spirosilole. Palladium chemistry was then used to introduce further functionality to the spirosilole, for example, to form **52** (Figure 12). The performance of OLEDs based on the silole materials has been found to be sensitive to the variations in the light-emitting silole structure. The more heavily derivatised spirosilole materials were less luminescent in the solid state than the parent silole, giving rise to less efficient devices although this may also be in part due to the different device structures. For example, an OLED containing **52** (ITO/NPB/**52**/LiF/Al) [NPB = *N*,*N*′-bis(1-napthyl)-*N*,*N*′-diphenylbenzidine] had a moderate efficiency of 2.0 cd/A at a brightness of 4350 cd/m^2.[192] In contrast a device containing **53**, which is similar to **52** but without the tetraphenylspirosilole, gave yellow-green emission with a maximum efficiency of 27 Cd/A and 6 lm/W in a single layer device (ITO/PEDOT/**53**/Ca)[194] while introduction of one or two (**54** in Figure 12) carbazoles onto the phenyl rings attached to the silicon atom reduced the aggregate-enhanced emission and gave less luminescent materials and OLEDs.[194] Interestingly, **54** blended with Alq_3 has also been used in a PV cell (ITO/NPB/Alq_3:**54**/Alq_3/LiF/Al), giving an η of up to 2.2% at low illumination power.[194]

7. Conclusions

The application of dendrimers to new technology areas continues to grow apace. While very large dendrimers have been made, such high-generation materials are probably not needed for many applications and especially for optoelectronic applications. The branched structure and modular synthesis nature of dendrimers means that the required functionality can be introduced at low generations. This has been vividly demonstrated with charge-transporting and light-emitting dendrimers that have been used in OLEDs. The chemistry used to synthesize the optoelectronic dendrimers is generally straightforward, and utilization of the convergent route ensures that surface groups are present to provide solubility during both the synthesis and the processing and ensures that there are no reactive functional groups remaining that can lead to device degradation. In comparing the device performance of well-defined dendrimers versus highly branched materials at this stage, the former have given the superior performance in device applications. While the development of light-emitting dendrimers is much advanced and has now reached the stage where they are considered as the third class of light-emitting materials, their use in other applications is still in its infancy and there is much yet to be explored and developed. In particular, for each application, the shape, generation, and components of the dendrimer need to be optimized to overcome the factors that limit device performance. In addition, while the work on light-emitting dendrimers has shown that high-efficiency devices can be formed, it is important to recognize that the efficiency of performance is only one factor and that the devices must also have commercially relevant lifetimes. This latter aspect is one of the great challenges to making dendrimers technologically relevant for semiconductor applications.

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