# Dendritic macromolecules for organic light-emitting diodes

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Received 12th May 2008

First published as an Advance Article on the web 11th September 2008 DOI: 10.1039/b803932c

The general concepts, design criteria, and physical parameters, such as component placement and electroluminescence, that relate to the construction of OLED devices are described, followed by a discussion of the current literature detailing the use of branched and dendritic materials as the key electroluminescent elements of single- and multi-layered fabricated devices. Their configurations, efficiencies, emission intensities, and molecular structural implications are also delineated and discussed. This critical review should appeal to researchers in the synthetic, material, and physical sciences (122 references).

# 1. Introduction

Electroluminescence (EL) was observed for the first time with inorganic compounds (ZnS phosphors) as early as 1936 by Destriau.<sup>1</sup> The discovery in 1947 that a transparent anode could be constructed by depositing a layer of indium tin oxide (ITO) onto a glass surface opened the possibility of obtaining light-emitting planar surfaces.<sup>2,3</sup>

EL for an organic semiconductor was first reported in 1963 by Pope *et al.*;<sup>4</sup> however to obtain the emission, large voltages, typically 400 V, were required. In 1965, similar studies were reported by Helfrich and Schneider<sup>5</sup> using liquid electrodes. Accordingly, an understanding of the EL process was developed that consisted of the injection of electrons in one electrode and holes in the other, along with the radiative decay of an excited state, which was produced by the recombination process.

During 1987–1989, the seminal work of Tang and Van Slyke<sup>6</sup> demonstrated efficient EL in a two-layer, sublimed molecular film device comprised of a hole-transporting layer of an aromatic

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diamine and an emissive layer of tris(8-hydroxyquinoline) aluminum (Alq3). This result provided a basic design for the LED architecture, which was applicable to systems employing low molecular weight electroluminescent materials either neat or in an inert polymeric matrix, such as electro-optically active polymers or copolymers.

Other advances included vacuum deposition of amorphous transport layers separating the polycrystalline materials from the electrodes<sup>6,7</sup> and dispersing the chromophores in a polymeric matrix.<sup>8</sup>

These breakthroughs initiated the development of new molecular materials and device structures. Since the end of the 1990s, organic light emitting diodes (OLEDs) have entered the commercial stage and are considered to be promising candidates for such uses as the next generation of large area flat-panel displays.<sup>9,10</sup> Numerous reviews on electroluminescent polymers focusing the basic physics, $1^{1-13}$  synthesis and properties, $^{14}$  device operation and materials, $^{15,16}$  design and synthesis of blue emitting structures<sup>17</sup> have appeared. Some books are also available on this subject.<sup>18,19</sup> Although

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some key reviews on OLED applications involving dendrimers have recently appeared, $20,21$  herein we will focus on lightemitting device performance constructed using macromolecules derived from dendrons, dendrimers, hyperbranched polymers, and dendronized polymers.

# 2. Principles of electroluminescence

Organic thin films used for OLEDs usually consist of multiple organic and metallic layers on an ITO-covered glass plate. These layers may be deposited by various methods, such as: plasma deposition, thermal evaporation, Langmuir–Blodgett deposition or spin casting from solutions. All these layers should be chemically stable, especially under the device's operating conditions, and resistant to oxidation. In addition, the optical properties of each layer should be considered when designing the device's structure. For higher efficiency light output, the device layers should be highly transparent to the emitted radiation.

Except for the anode and cathode, electroluminescent devices may contain single- or multiple-layered structures. The single-layer device consists of a single organic layer sandwiched between the anode and cathode. In this case, the organic layer serves as the emitting source for the device and should therefore have a relatively high photoluminescence quantum efficiency. This emissive layer must also have good bipolar charge-transport properties, which are necessary for the transport of holes and electrons through the organic layer. These holes and electrons, driven into the emitting layer by the applied electric field, will later recombine on the emitter molecules to form singlet and triplet excitons. To forward the bias, the light emitting diode (LED), the anode, comprised of usually high-work-function materials, such as ITO, is connected to a positive potential. Low-work-function metals, e.g., calcium, magnesium, aluminum or alloys, such as Mg:Ag, are used as the negative electrode (cathode). Electron transport will occur through the lowest unoccupied molecular orbital (LUMO), which is analogous to the conduction band  $(E_c)$  in semiconductors. Holes are transported through the highest occupied molecular orbital (HOMO), which corresponds to the valance band  $(E_v)$  in semiconductors. The efficiency of electron and hole transport is determined by the mobilities of both the charges in the organic layer.

Instead of using single-layer structures, additional layers can be added to the OLED to improve charge transport and injection. In a multilayer device, the layers may consist of the anode, hole-transport layer (HTL), emission layer (EML), electron-transport layer (ETL), and cathode.

## 3. General structure and device performance

## A Dendrons and dendrimers

Dendrimer research was initially created<sup>22,23</sup> in the mid 1980s and has exploded during past two decades. Their stepwise (divergent and convergent)<sup>24</sup> syntheses allow the selective grafting of the desired (core, branches and surface) functional groups to impart particular properties<sup>25</sup> including: lowdielectric materials<sup>26</sup> and templates for the growth of single-wall carbon nanotubes,<sup>27</sup> catalysis,<sup>28–30</sup> and biological

applications $3^{31-34}$  including biosensors,  $3^5$  magnetic resonance imaging, $36-38$  and drug delivery.<sup>39–42</sup> Among these functional groups, fluorescent entities occupy a special place, since they have been grafted to several types of dendrimers and for different purposes, including analytical uses such as the detection of dendritic defects or the measurement of hydrodynamic radius, and also for applications such as labeling of biological entities or elaboration of electroluminescent materials exploitable as light-emitting diodes. Indeed, OLEDs have key advantages for full-color flat-panel displays, such as high luminescence efficiency, color purity, wide viewing angle, low weight, and lower drive voltages. Initially, we will describe the brief development of dendritic materials for OLEDs.

In this OLED arena, arylalkene-based dendrimers have been one of the most widely studied families of dendrimers with *trans*-stilbenyl branching frameworks playing a major role in the structures. Samuel and co-workers<sup>43</sup> demonstrated a hetero-layer OLED device using the 2nd generation (G2) conjugated dendrimer, as the light emitting molecule. The device consists of a graded bilayer structure formed from a neat dendrimer film covered with a film consisting of the same dendrimer but doped with the electron-transporting material 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (ph-PBD). The optimized dendritic OLED device with ph-PBD showed a peak electroluminescence external quantum efficiency of  $0.16\%$  at 600 cd m<sup>-2</sup>. This result means that the device's EL quantum efficiency is a factor of eight larger than that of a conventional bilayer LED made with the conjugated dendrimer, as the emissive layer, and poly(methyl methacrylate) doped with ph-PBD, as the electron-transporting layer. Notably, this deposition procedure greatly simplifies the manufacturing process. The controlled charge carrier confinement and the removal of the heterojunction interface in these graded devices significantly improve the device efficiency.

Four generations (G0–3) of conjugated dendrimers consisting of a 1,3,5-tris(distyrylbenzenyl)benzene core, stilbene dendrons, and tert-butyl surface groups were synthesized by Burn and co-workers $44$  and tested as light-emitting materials. All four generations of these dendrimers have been prepared by coupling a bisphosphonate with an appropriate aldehyde via a Wittig–Horner reaction. The degree of aggregation strongly depends on dendrimer generation. Comparison of the properties of these benzene-cored dendrimers with an equivalent family possessing a nitrogen atom, as the core, showed that the aggregation of dendrimers is related to the degree of delocalization across the core unit. Therefore, the dendrimer having the benzene core has a stronger aggregation in the solid state than those possessing the nitrogen core. The simple LED devices, ITO/poly(3,4-ethylenedioxythiophene) (PEDOT)/dendrimer/Al, prepared from the G0 and G1 dendrimers, were found to be less stable than devices derived from the G2 and G3 dendrimers. From these unoptimized devices, the external quantum efficiency was at best 0.002% for the G3 dendrimer. The EL spectra indicated that progressing from the 0th to 2nd generation, there was an increase in the emission at long wavelengths, but a decrease was observed for the 3rd generation. These trends clearly demonstrated the role of generation in controlling the intermolecular interactions.

Conjugated dendrimers consisting of a distyrylbenzene core (short wavelength emission), stilbene dendrons (charge transport), and tert-butyl surface groups (good processability) for light emitting materials were also synthesized (Fig. 1).<sup>45</sup> A single dendrimer layer LED device, ITO/dendrimer/Ca, was fabricated for testing. A visible blue light emission was observed from each of these materials. Devices derived from dendrimers 2 and 3 were more stable than those of dendrimer 1. The  $(x, y)$  chromaticity coordinates of observed emission were (0.34, 0.38) for 1, (0.29, 0.32) for 2, and (0.23, 0.24) for 3. The current through the devices showed diode-like characteristics for all generations, although current anomalies at low bias were often observed for devices based on the G1 (1) and G3 (3) dendrimers. The characteristics of G2-based devices were diodelike, and no current anomalies were observed in the majority of cases. The external quantum efficiencies of single layer devices were found to be 0.01, 0.07–0.09 and 0.03% for 1–3, respectively.

A small, branched stilbenoid construct, described as a dendrimer and possessing alkoxy termini, displayed blue emission (2.8 eV) when spin cast into thin films.46 Absorption and emission spectra of thin films prepared using toluene, THF,  $C_6H_5Cl$  and CHCl<sub>3</sub> were analyzed and compared to molecule spectra obtained from a  $10^{-5}$  M solution of CHCl<sub>3</sub>. Spectral properties were shown to depend on film morphology and dendrimer aggregation with inter-dendrimer interactions leading to absorption band broadening. Films obtained using CHCl<sub>3</sub>, as the solvent, exhibited the greatest emission efficiency.

Samuel and co-workers<sup>47</sup> synthesized the triphenylaminebased dendrimers decorated by three distyrylbenzene chromophores and demonstrated that the degree of interaction between chromophores relating to the packing of the molecules is controlled by the generation (Fig. 2). The LED device consisted of an ITO/PEDOT/dendrimer/Al sequence layer. The turn-on field for current flow more then doubles

proceeding from lower to higher generation (i.e., 4–6) demonstrating that the film became more insulating. The stability and lifetime of the device greatly increased as the generation increases; for G0 (not shown), current anomalies are frequently observed, which were not apparent at higher generations. EL was detected at an applied bias of 4 V for all generations, but the increase with field becomes more gradual as the generation increased. Modified dendrimers with meta-linked biphenyl units, as dendrons, emit green light by using bilayer devices with a blurred interface, which was fabricated by sequentially spin-coating a neat dendrimer and a dendrimer doped with 2-(4-biphenyl)-5-(4-tert-butylphenyl)- 1,3,4-oxadiazole (PBD). By optimizing the concentration of PBD, the maximum brightness and EL quantum efficiency reached 4100 cd  $m^{-2}$  and 0.17%, respectively, which are the best results reported so far for OLEDs using dendrimers as an active material with an Al cathode.<sup>48,49</sup>

Three new electron-acceptor and light-emitting conjugated dendrimers, based on an aryl core, poly(phenylenevinylene) dendrons, and diphenylquinoline peripheral groups have been synthesized by Jenekhe and co-workers $50$  As the emissive materials in LEDs, the dendrimers showed a yellow EL whose brightness and efficiency increased with dendritic generation and number of electron-acceptor peripheral groups. The performance of bilayer LED using the dendrimers, as the electron-transport layers, and the emissive poly[2-methoxy-5- (2'-ethylhexyloxy)-1,4-phenylenevinylene] layer also increased with generation and number of electron-acceptor peripheral groups, reaching a maximum external efficiency of 5.0%, a power efficiency of 1.3 lm  $W^{-1}$ , and a brightness of up to 2000 cd  $m^{-2}$  in ambient air using Al cathode. These results demonstrated that electron-acceptor and -transport can be introduced and controlled by functionalization of the dendrimer's periphery.



Fig. 1 Conjugated dendrimers (1–3; G1–3) consisting of a distyrylbenzene core, stilbene dendrons, and tert-butyl surface groups.



Fig. 2 Nitrogen-cored distyrylbenzene dendrimers (4–6; G1, G2 and G3).

Burn and co-workers<sup>51</sup> modified a new distyrylbenzenecored dendrimer, which utilizes triazine rings to link the surface groups. Single-layer LEDs were fabricated to give the ITO/dendrimer/Ca system. It can be seen that the current turn-on occurs before any light is emitted and that the current flow is very noisy due to poor chemical stability. The late onset of the light output with respect to the current flow is indicative of a strong imbalance between the charge carriers, which is likely to arise from both unbalanced motilities and a difference in barrier heights to injection. The devices external quantum efficiency is correspondingly low and was measured to be in the order of 0.003%. This result is similar to that reported by Halim et al.<sup>45</sup> for a G1 distyrylbenzene dendrimer with stilbene dendrons in the same device configuration, which is comparable to that of a PPV single layer device with Al contacts. The EL was found to be at best 1 cd  $m<sup>-2</sup>$  at 10 mA  $\text{cm}^{-2}$ ; however, the device's characteristics changed, as the device was run repeatedly and current–voltage characteristics displayed symmetrical ohmic behavior in the low forward and reverse bias region, which could be due to the formation of conductive pins or chains through the film. A possible explanation is the diffusion of Ca through the material.

Several 2,7-dibromofluorene monomers, attached to benzyl ether dendrons  $(G1-3)$  at the 9,9'-position of the fluorene ring, were synthesized and employed in condensation polymerizations to afford both homopolymers and copolymers with diethylhexylfluorene by Carter and co-workers.<sup>52</sup> The device configuration is ITO/PEDOT/dendritic polymer/Ca/Al, which was accomplished by spin-coating from *p*-xylene solution, followed by stepwise evaporation of the Ca/Al cathode onto the EL-active layer. The diodes with the G1 and G2 dendronized 2,7-PF homopolymers emit blue light at ca 16 V. The

LED built from the corresponding copolymers showed considerably lower turn-on voltages of 4.6 and 6 V due to device stability.

Tao and  $\cos^{-3}$  reported a series of starburst hexadiarylamines with hexa(thienyl)benzene, as the core, prepared from hexabromobenzene and different diarylaminothienyl stannanes by the Stille cross-coupling reaction. These materials form stable glasses with  $T_g$  values between 80 and 111 °C and are easily oxidized to multication salts at potentials about 150 mV lower than that required for conventional triphenyldiamines (TPDs). Two-layer EL devices with these compounds, as hole conductors, and  $Alg<sub>3</sub>$ , as emitter, ITO/HC  $(40 \text{ nm})/Alg_3$   $(46 \text{ nm})/Mg:Ag$  possess turn-on voltages of  $6-8$  V, external quantum efficiencies of  $1.2-1.6\%$ and maximum luminescence of  $14-20 \times 10^3$  cd m<sup>-2</sup>.

Wong et al.<sup>54</sup> synthesized blue-emitting distyrylstilbenes (DSBs) bearing various electron or hole affinitive moieties including oxadiazole, cyano, and propoxy on the outer surface of the G1 and G2 poly(benzyl ether)-type dendritic wedges at either one or both ends. The single-layer light-emitting diodes using dendritic DSB doped  $poly(N-viny)$  (PVK) film, as an emissive layer, with a structure of ITO/ DSB:PVK/Al have been fabricated and investigated. The LEDs based on the 'asymmetrically' dendron-substituted DSBs exhibit a better performance than devices crafted from the corresponding 'symmetrical' counterparts. Device performance of the G1 dendritic DSB doped single-layer LEDs was generally superior to that of the corresponding G2 dendrimerbased devices.

Müllen and co-workers<sup>55</sup> designed and prepared soluble perylene-3,4,9,10-tetracarboxydiimide (PDI) derivatives bearing alkyl-substituted pentaphenylene dendrons at the



Fig. 3 Perylene-3,4,9,10-tetracarboxydiimides with aromatic, dendritic arms attached to the bay positions.

bay positions, since in the solid state aggregation of chromophores can cause undesirable red shifts in the emission spectra and/or emission quenching (7 and 8; Fig. 3). Single-layer LEDs produce a red-orange emission with relatively low

efficiency especially for the higher generation dendrons, which is attributed to poor charge conduction.

Tian and co-workers<sup>56</sup> synthesized naphthalimide dendrimers using a combined convergent and divergent approach (9–13; Fig. 4). The dendrimers consisted of naphthalimide-based cores, Fréchet-type poly(aryl ether) dendrons, and carbazole or oxadiazole peripheral groups to improve the charge carriertransporting property for the OLED applications. This configuration enhanced the processing and electronic properties and could be independently tuned. EL devices with an ITO/ PEDOT/dendrimer/Ba/Al configuration as well as G1 and G2 dendrons having carbazole peripheral groups have external quantum efficiencies of 0.5 and 0.02% and maximum luminescence of 308 and 59 cd  $m^{-2}$ , respectively. Dendrimers containing perylenediimide cores, Fréchet-type poly(aryl ether) dendrons, and carbazole (CZ) or oxadiazole (OXZ) peripheral functional groups were synthesized.<sup>57</sup> For the dendrimers bearing carbazole units, the fluorescence arises by two possible mechanisms: Förster energy transfer (FRET) and photoinduced electron transfer (PET). This means that no enhanced core fluorescence is observed, since the energy transfer of lightharvesting potential of the peripheral carbazoles is counteracted by PET. However, the dendrimers bearing oxadiazole units do not show the PET phenomena between OXZ and perylenediimide, since both possess high electron affinity. The single-layer LED devices using the dendrimers, as the active layer, with the ITO/PEDOT/dendrimer/Ba/Al configuration were fabricated. The device utilizing dendrimer 2CZ-PTCDI (G0) has the maximum brightness of 85.4 cd  $m^{-2}$  at 10 V; whereas, dendrimer 8CZ-PTCDI (G2) has the highest external quantum efficiency  $(0.105\%)$ . The turn-on voltage of the 8CZ-PTCDI device is ca. 4 V higher than those derived from the G0- and G1-dendrimers suggesting that the larger dendron shell has a larger influence on the trapping process.<sup>55</sup>



Fig. 4 Dendrimers constructed with naphthalene cores, Fréchet-type poly(aryl ether) dendrons, and carbazole or oxadiazole peripheral functional groups.



Fig. 5 Oligo(thiophene)-based dendrimers for use in solar cell and OLED applications.

Carbazole-based dendrimers attached to oligothiophene cores with triarylamine termini have also been reported<sup>58</sup> with potential for application in solar cell and OLED devices (14; Fig. 5). Second generation constructs were employed as hole-transporting emissive layers in OLEDs along with 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI), as a hole-blocking layer; LiF/Ag was used for the cathode. 4 V turn-on voltages were achieved where a dithiophene (DPT) core and a corresponding pentathiophene (PTP) core afforded blue and yellow electroluminescence, respectively. The highest luminance observed was 1000 cd m-<sup>2</sup> at 19 V. Oligomeric macrocycles constructed from triphenylamine and oligofluorene units were also examined for use as hole-transporting emissive layers.<sup>59</sup>

Fréchet and co-workers<sup>60</sup> have designed a single-layer multichromophoric OLED using the site isolation of two dyes, i.e. Coumarin 343 (C343) and pentathiophene (T5), capable of electronic interaction via Förster energy transfer. Freeman et al.<sup>61</sup> successfully utilized triarylamine (TAA) holetransporting labeled poly(benzyl ether) dendrimers possessing C343 and T5 core dyes to give blue and green OLEDs, respectively. Initial attempts to achieve synergistic emission from the two types of dendrimers by blending them into a single layer were moderately successful due to detrimental energy transfer from C343 to T5 possessing the smaller band-gap. Due to the large Förster radius of these dyes, energy transfer is an unfortuitous consequence of the small size and flexibility (i.e., poor shielding effect) of the surrounding dendrons that are attached at a single point to the lumophores. The OLED devices possessing the ITO/PEDOT:PSS/  $[GAC : G5T (x : y)]/PBD/BCP/AlQ<sub>3</sub>/LiF/Al$  configuration were fabricated by spin-coating. The maximum external quantum efficiency of the mixed G4C : G5T (5 : 1) device was 0.2% with a power efficiency of 0.1 lm  $W^{-1}$ . The device had a turn-on voltage of *ca*. 12 V and a maximum luminescence of only 22 cd  $m^{-2}$  at 20 V. Device performance data for an OLED, prepared from the G5T alone, had much better characteristics; a maximum luminance of 420 cd  $m^{-2}$  was recorded at 20 V. The device had a maximum efficiency of 0.59 lm  $W^{-1}$  (0.76% photon/electron) at a brightness of 100 cd  $m^{-2}$ . Using the dendrimer containing 12 triarylamine (TAA), as hole transport, the dyes, C343 and T5 were coated.<sup>61</sup> The single-layer devices, ITO/dendrimer-PBD/ Mg:Ag/Ag, were fabricated. Most of the devices had turn-on voltages between 12–15 V and could be driven at voltages exceeding 30 V.

Pei and co-workers<sup>62</sup> have designed the G0, G1  $\pi$ -conjugated dendrimers based on 10,15-dihydro-5H-diinde $no[1,2-a;1',2'-c]$ fluorene (truxene) using the acid-promoted cyclotrimerizations from acetyl aromatics to generate the benzene cores (15; Fig. 6). The device was fabricated to give a ITO/PEDOT-PSS/dendrimer/Ba/Al configuration. Both the dendrimers emitted a blue-green color at a forward bias  $> 8$  V. The external quantum efficiencies were measured to be 0.16% at 27 V for G0 and 0.16% at 13 V for G1.

Levermore et al.<sup>63</sup> constructed rigid, conjugated dendrimers possessing a triazatruxene core and oligo(fluorene) branches (16; Fig. 6) that exhibited a deep-blue emission [1931 CIE  $(x, y) = (0.15, 0.10)$  and high luminance (<6000 cd m<sup>-2</sup>). OLEDs were prepared based on binary blends for the emissive layer of the dendrimer with a green light emitting polymer [poly(9,9-dioctylfluorene-co-benzothiadiazole)]. This device was characterized by a low turn-on voltage  $(>2.2 V)$  and high efficiency green EL (18.2 lm  $W^{-1}$  at 100 cd m<sup>-2</sup>).

Using the repetition of two steps (a nucleophilic substitution of hydroxybenzaldehyde on  $P(S)Cl<sub>2</sub>$  groups and a condensation reaction of a phosphorhydrazide with the aldehydes),  $64$ several series of P-dendrimers decorated by potential fluorescent end groups (naphthalene, anthracene, and pyrene) have been synthesized by Majoral, Caminade and co-workers.<sup>65</sup> Among them, the G1–4 P-dendrimers decorated by pyrene have been tested for the elaboration of OLED using the ITO/ dendrimer:PVK/Ca/Al configuration. In the case of the materials elaborated from these P-dendrimers, the threshold tension  $(V_t)$  is very high (18 V for G1 and G3 and 20 V for G4). These high values might be due to electron trapping within the dendritic structure. The best result of luminance was shown by the G4 device as only 3.5 Cd  $m^{-2}$ .



Fig. 6  $\pi$ -Conjugated dendrimers based on rigid, truxene (15) and triazatruxene (16) units.



Fig. 7 Cyclic phosphazene-cored dendrimers possessing aminopyrene moieties.

Bolink *et al.*<sup>66,67</sup> have reported the construction of solution processable, G1, cyclic phosphazene-cored dendrimers possessing aminopyrene moieties (17–18; Fig. 7) and subsequently used them as emissive layers in OLEDs. ITO/PEDOT:PSS/ dendrimer/TPBI/Ba/Ag device configuration resulted in photoluminescent quantum efficiencies ranging from 0.67 to 0.83 with the phenyl extended constructs giving higher efficiencies relative to the biphenyl extended materials. Green to blue emission was observed with a deep blue exhibited upon mixing the dendrimer with small quantities of a hole and electron transporting matrix.

Dominguez-Chávez et al.<sup>68</sup> have also reported the creation of fluorescent materials (G1–G3) based on oligo(phenylenevinylene) cores that exhibited blue emission in solution with a  $\lambda_{\text{max}}$  = 444–446 nm. The G2 construct yielded the most homogeneous films and also the highest quantum yield in solution.

#### B Metallodendrimers

Since phosphorescent molecules have shown a good efficiency in OLEDs, many researchers have become interested in metallodendrimers, as potential phosphorescent emitters. Thus, transition-metal complexes, particularly those containing  $Pt(II)$  and  $Ir(III)$ , have served as efficient phosphorescent

emitters.<sup>69–71</sup> In such systems, holes and electrons are injected at opposite surfaces of the planar multilayer organic-thin film stack. The holes and electrons migrate through the thin films to the interface between the two layers, where they recombine to form radiative excited states, or excitons. This electrically generated excitement can be either a singlet or triplet.<sup>72</sup> Theoretical predictions and experimental measurements agree on a singlet-to-triplet ratio for these excitons of  $1 : 3.^{73-77}$  Both the singlet and triplet excited states can be trapped at the phosphorescent emitter, leading to devices with high efficiencies. OLEDs prepared with transition-metal complexes, such as  $Ir(III)$  or  $Pt(II)$  complexes, are the most efficient OLEDs reported to date, with theoretical internal quantum efficiencies of 100%78 due to harvesting both singlet and triplet excitons.<sup>79–81</sup> In the following section, we highlight recent developments in OLED technology based on the metallodendrimer, as the phosphorescent emitter.

Cheng, Wang and co-workers<sup>82</sup> created green-emitting, iridium dendrimers with rigid hole-transporting carbazole dendrons and investigated the integration of the holetransporting carbazole dendrons and Ir(III) complexes, for designing promising solution-processable phosphorescent materials for OLED applications (19–21; Fig. 8). With the G2 dendron 21, the photoluminescence quantum yield was up to 87% in solution and 45% in a film. Devices with the configuration ITO/PEDOT:PSS/20 or 21/Ca/Al showed low efficiency (maximum luminous efficiency of 0.30 cd  $A^{-1}$ ) due to poor electron-injection and electron-transport capabilities of carbazole dendrons. However, for devices with a ITO/PEDOT:PSS/20 or 21/TPBI/LiFAl configuration, a maximum external quantum efficiency (EQE) of 6.8 and 10.3%, a maximum brightness of 6570 and 7840 cd m<sup>-2</sup>, and a maximum luminous efficiency of 23.2 and 34.7 cd  $A^{-1}$ for G1 and G2, respectively, were realized.

The Burn's group<sup>83</sup> synthesized a metallodendrimer consisting of a fac-tris(2-phenylpyridine) iridium core, phenylene dendrons, and 2-ethylhexyloxy surface groups. This device was prepared using a neat solution-processed method consisting of an iridiodendrimer emissive layer with an evaporated 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinebased (BCP) electron-transport/hole-blocking layer. This unique metallodendrimer device exhibited a bright green luminescence with a turn-on voltage of 4.5 V and peak brightness of 1680 cd  $m^{-2}$  at 12 V but the maximum efficiency of the device was, however, low [0.14 lm  $W^{-1}$  (0.47 cd  $A^{-1}$ ) at 9.5 V]. Blend devices such as ITO/IrppyD:CBP:BCP:LiF/Al, ITO/ IrppyD/TCTA/BCP/LiF/AlandITO/IrppyD:TCTA/TPBI/LiF/Al have also been examined; where, IrppyD is the metallodendrimer, CBP is 4,4'-bis(N-carbazolyl)biphenyl, TCTA is 4,4',4"-tris(N-carbazolyl)triphenylamine, and TPBI is 1,3,5-tris(2-N-phenylbenzimidazolyl)benzene. It was observed that the efficiency of these devices remained relatively constant over a range of brightness. This resulted from a balanced charge injection and uniform distribution of iridiodendrimer in the host layer.

A simple convergent procedure has been applied to the preparation of the solution-processable phosphorescent metallodendrimers with biphenyl-based dendrons and  $fac\text{-}tris(2\text{-}phenylpyridyl)iridium(III) cores.<sup>84</sup> The attachment$ 



Fig. 8 Ir(III)-metallodendrimers with carbon–metal bonds (19–21).

point and branching of the dendrons were important for controlling the color of the light emission. The photoluminescent quantum yield of the neat metallodendrimer film increased with increasing generation suggesting the ability of the metallodendrimer architecture to control intermolecular interaction. Recently, the modified fac-tris(2-phenylpyridyl) iridium(III)-cored metallodendrimers using phenylene- and carbazole-based dendrons with 2-ethylhexyloxy surface groups were reported<sup>85</sup> (22 and 23; Fig. 9). By studying the triplet–triplet annihilation in neat film state, the triplet exciton diffusion length varied in the range of 2–10 nm depending on dendron size. Also, the estimated current densities for triplet–triplet annihilation to half the efficiency of a metallodendrimer LED was less than  $1 \text{ A cm}^{-2}$ . The nearest-neighbor hopping rate exponentially decreased with intermolecular spacing indicating that energy migration was dominated by the exchange mechanism. As well, fac-tris(2-phenylpyridyl) iridium(III) core metallodendrimers containing Müllen dendrons were synthesized (24 and 25) and compared to the physical, optoelectronic, and device properties with the metallodendrimers mentioned above.<sup>86</sup> Because of their poor solubility, the simple single-layer devices [ITO/dendrimer  $(25 \text{ wt\%})$ :CBP/Ca/Al] were shown to have a turn-on voltage  $(1 \text{ cd } m^{-2})$  of 7.6 V, and the maximum external quantum efficiency was 2.9% (9.3 cd  $A^{-1}$ ) with a power efficiency of 1.9 mW at a brightness of 1545 cd  $m^{-2}$  and 15.6 V. The fact that the highest efficiency occurs at a high drive voltage suggests that there is charge imbalance. Recently, fac-tris-(2-phenylpyridyl)iridium(III) core metallodendrimer possessing highly branched biphenyl dendrons was reported.<sup>87–89</sup> The presence of fluorene surface groups improved the solubility and enhances the efficiency of photoluminescence, especially in the solid state. Device performance was significantly improved by the incorporation of an electron-transporting layer of 1,3,5 tris(2-N-phenylbenzimidazolyl)benzene. A peak external quantum efficiency of 10% (38 cd  $A^{-1}$ ) for the metallodendrimer without surface groups and  $13\%$  (49.8 cd  $A^{-1}$ ) for the metallodendrimer with fluorene surface groups is achieved in

the bilayer device configuration with ITO/metallodendrimer : CBP (2 : 8)/LiF/Al.

The pure red-emitting bifunctional  $Ir(III)$  metallodendrimers with G0-2 triphenylamine dendrons were reported.<sup>90</sup> Using these metallodendrimers, deep-red devices were fabricated in the ITO/PEDOT:PSS/ $x\%$  of metallodendrimer:CBP/Alq<sub>3</sub>/ LiF/Al configuration. All of these devices emit pure red light with an electroluminescence maximum at *ca*. 640 nm and excellent CIE color coordinates of (0.70, 0.30). The best device performance using the G1 metallodendrimer is with a doping level of 8 wt%. The device has a turn-on voltage of 4.4 V, a maximum brightness of 7451 cd  $m^{-2}$  at 17 V, an external quantum efficiency of 11.65% at 5 V, a luminance efficiency of 5.82 cd  $A^{-1}$  at 5 V, and a power efficiency of 3.65 lm W<sup>-1</sup> at 5 V. While the device using 10 wt% of the G2 metallodendrimer showed the best performance, with a turn-on voltage of 4.7 V, a maximum brightness of 6143 cd  $\mathrm{m}^{-2}$  at 16 V, and external quantum efficiency of 7.36% at 6 V, a luminance efficiency of 3.72 cd  $A^{-1}$ , and a power efficiency of 2.29  $\text{Im } W^{-1}$  at 5 V.

Tokito and co-workers $91$  synthesized the G1 and G2 metallodendrimers consisting of a  $fac\text{-}tris(2\text{-}phenylpyridyl);iridum(III)$ core and hole-transporting phenylcarbazole-based dendrons. The OLEDs using a film containing a mixture of the iridium $(m)$ metallodendrimer and 1,3-bis[5-(4-tert-butylphenyl)-1,3,4 oxadiazol-2-yl]benzene, as an electron-transporting material, exhibited higher efficiency than those using the neat metallodendrimer film. The current for a given voltage is higher in the OLED using neat G1 than those in the OLEDs using the dendrimer consisting of the  $Ir(ppy)$ <sub>3</sub> core and phenylene-based dendrons $92$  indicating that the hole drift mobility of the dendrimer was improved by using hole-transporting dendrons. However, the OLED using the neat G2 showed less current and higher turn-on voltage than that of neat G1.

Tian et al.<sup>93,94</sup> synthesized the dendritic europium complexes containing terminal grafted carbazole units. Under the indirect excitation of the carbazole units, a characteristic red emission peak at 615 nm due to the Eu(III) ion transition of <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub> was



Fig. 9 fac-Tris(2-phenylpyridyl)iridium(III)-cored metallodendrimers containing phenylene-based dendrons with 2-ethylhexyloxy surface groups  $(22$  and  $23)$  and Müllen dendrons  $(24$  and  $25)$ .

observed for the complexes in either solution or solid films. As a result of the light-harvesting and site-isolation of carbazole dendrons, compared with the reference  $[Eu(BPPD)_{3}(phen)]$ , photoluminescence efficiencies of [Eu(MCPD)<sub>3</sub>(phen)],  $[Eu(BCPD)_{3}(phen)]$  and  $[Eu(TCPD)_{3}(phen)]$  in the film state have 3.3, 7.9 and 4.5 fold increase, respectively; where, BPPD is 1-[3,5-bis(phenylmethoxy)phenyl]-3-phenylpropan-1,3-dione, MCPD is 1-{4-[4-(9H-carbazol-9-yl)butoxy]phenyl}-3-phenylpropan-1,3-dione, BCPD is 1-{3,5-bis[4-(9H-carbazol-9-yl) butoxy]phenyl}-3-phenylpropan-1,3-dione, TCPD is 1-{3,4,5 tris[4-(9H-carbazol-9-yl)butoxy]phenyl}-3-phenylpropan-1,3 dione, and phen is 1,10-phenanthroline. The EL device, ITO/ NPB/CBP:Eu(TCPD)3(Phen)/BCP/Mg:Ag, showed a white light emission with the CIE coordinates of (0.333, 0.348); where, NPB is  $N, N'$ -bis(1-naphthyl)- $N, N'$ -diphenyl-1,1'diphenyl-4,4'-diamine. Its maximum external quantum efficiency was more than 1.1% and maximum brightness reached 229 cd  $m^{-2}$ . The origin of the blue and green emission was attributed to the dendron-grafted carbazoles forming an exciplex and electroplex with CBP and ligand  $\beta$ -diketone, respectively. These results suggested that the modifying ligand can not only tune the carrier-transporting properties of complexes, but also provided a useful clue to the use of electroplexes or exciplex to realize broad or even white electroluminescence.

Yamamoto and co-workers<sup>95</sup> have designed and synthesized a series of G1 and G2 diphenylamine-substituted phenylazomethine dendrimers, (26–29; Fig. 10) as hole-transport materials for OLEDs. After construction of the dendrimers, they were complexed with metal ions. These systems show good multi-redox properties attributed to the terminal amine moieties and excellent thermal stabilities; a two-layer EL device was fabricated with ITO/dendrimer/Alq3/CsF/Al. The luminance and efficiency characteristics of these devices increased with generation not only for the device using the dendrimers but also for the device using an aniline-termini. All devices showed a turn-on voltage (at 0.1 cd  $\text{m}^{-2}$ ) below 4.0 V. The maximum luminance (1314 cd  $m^{-2}$  at 9.0 V) and the maximum efficiency (0.30 lm  $W^{-1}$  at 6.0 V) of the device of the G2 dendritic counterpart are similar to those of the G2 dendrimer without the aniline surface. However, the EL performances of metal ion complexed dendrimers were drastically increased. The device that used a metal-complexed (0.5 equiv.) dendrimer as the hole-transport layer, showed a maximum luminance (4400 cd  $m^{-2}$  at 9.0 V) and the highest EL efficiency (0.39 lm  $W^{-1}$  at 6.0 V). These results suggested that the metal-ion complexation of the imine sites resulted in an increasing hole injection or transporting efficiency or both from the electrode. Due to the changing energy gap of the layer, the ohmic conductivity of the layer was increased by



Fig. 10 Diphenylamine-substituted, phenylazomethine dendrimers used for metal complexation.

doping;  $96-98$  however with 1.0 equiv. metal ion, there was a drastic decrease in EL performance due to the formation of many dark spots on the emitting surface caused by aggregation or isolation or both of the complexed metal ions.

#### C Dendronized polymers

Research on dendronized polymers has developed into a new and growing field at the interfaces of organic chemistry, polymer synthesis, and material science, as can also be seen in the growing number of publications and recently published reviews.99–102 In fact, dendronized polymers are among the many interesting molecular and supramolecular structures developed over the past decade that have helped to blur the lines between these different disciplines. More recently, there has been a noticeable shift in emphasis. Many different synthetic strategies have been thoroughly explored, and their scope and limitations are well understood. Research is currently focusing on creating interesting structures and



Fig. 11 Dendronized polymers encapsulated by Müllen-type polyfluorene-based dendrons.

materials for utilitarian applications, while using the best synthetic strategies to obtain specific target structures. Dendronized polymers are used both in otherwise already established applications, e.g. organic materials for optoelectronic applications, and in engineering intriguing new concepts, which may only be accessible via these remarkable macromolecules.

The Müllen group<sup>103</sup> was the first to report an encapsulated linear polymeric emitter, polyfluorenes, by a dendritic structure (30; Fig. 11). This combination can serve as solubilizing groups in toluene, benzene and chlorinated organic solvents in order to permit spatial control of the polymer chain and to hinder aggregation. This polymer exhibited the same absorption and emission maxima as the alkyl-substituted polyfluorenes, which implies that the bulky groups in position 9 do not alter the torsion angle of the conjugated backbone. The ITO/PEDT:PSS/polymer/Ca/Al device showed a maximum luminance (400 cd  $m^{-2}$  at 10 V) and maximum efficiency  $(0.2 \text{ cd } A^{-1} \text{ at } 7.5 \text{ V})$ . These device-related parameters are very similar to those<sup>104</sup> fabricated from polyfluorene 31, except for their lower onset voltages. The polyfluorene, containing the shortened and more stable linkage between the main chain and dendron was also synthesized.<sup>105</sup> The device configuration of ITO/PEDOT:PSS/polymer/Ca/Al, exhibiting a deep blue color with CIE coordinates of (0.189, 0.237), was fabricated. This device showed a turn-on voltage of 6–7 V, a maximum efficiency of 0.06 lm  $W^{-1}$  at 7.8 V, and maximum luminance of 380 cd  $m^{-2}$ . To investigate the degradation of the device, it was continuously operated for 30 min at 8 V bias. Subtracting the EL spectrum of the unstressed device from that of the degraded device, the luminescence changed due to an additional emission peak at ca. 2.3 eV. This emission origin from ketonic defect sites was formed by oxidation under the operation;<sup>106</sup> however, the formation of this emission can be efficiently suppressed when operating the device using short electric pulses leading to reduced ohmic heating of the polymer. Additionally, the dendron side chains are known to suppress exciton migration as evidenced by time-resolved photoluminescence



Fig. 12 Dendronized polymers based on PPV.

measurements.<sup>107</sup> In this respect, this dendronized polyfluorene can be regarded as a solid-state solution. This is beneficial for the device's color stability since the excitons have a considerably diminished chance to migrate to a ketonic defect site and recombine there as this defect acts as a trap for the exciton.

Zou and  $co\text{-}works<sup>108</sup>$  have synthesized the conjugated  $poly(p$ -phenylenevinylene) derivatives bearing various dendritic pendants, e.g. poly{2-[3',5'-bis(2"-ethylhexyloxy)benzyloxy]-1,4-phenylenevinylene} (BE-PPV; 32),  $poly{2-[3', 5'-bis(3'',$ 7"-dimethyl)octyloxy]-1,4-phenylenevinylene} (BD-PPV; 33), poly-(2-{3',5'-bis[3",5"-bis(2"-ethylhexyloxy)benzyloxy]benzyloxy}-1,4-phenylenevinylene) (BBE-PPV; 33),  $poly(2-\{3', 5'-bis[3'',$  $5^{\prime\prime}$ -bis( $3^{\prime\prime\prime}$ , $7^{\prime\prime\prime}$ -dimethyloctyloxy)benzyloxy]benzyloxy}-1,4phenylenevinylene) (BBD-PPV; 33), and  $poly[(2-\{2\prime, 5\prime - bis[3\prime\prime},$  $5''$ -bis( $2''$ -ethylhexyloxy)benzyloxy]benzyloxy}-1,4-phenylenevinylene)-co-(2-{3<sup>0</sup> ,50 -bis[3<sup>00</sup>,5<sup>00</sup>-bis(3<sup>000</sup>,7<sup>000</sup>-dimethyloctyloxy) benzyloxy]benzyloxy}-1,4-phenylenevinylene)] (BBE-co-BBD-PPV; 1 : 1; 35) (32–35; Fig. 12). Double-layer OLED devices with the ITO/polymer/tris(8-hydoxyquinoline)aluminum/Mg:Ag/ Ag configuration have been fabricated, and shown to emit a

green–yellow light. The turn-on voltage of BE-PPV, BD-PPV, BBE-PPV, BBD-PPV and BBE-co-BBD-PPV (1 : 1) were ca. 5.6, 5.9, 5.5, 5.2 and 4.8 V, respectively. The LED devices of BE-PPV and BD-PPV possessed the highest electroluminescence performance; they exhibited maximum luminance with about 860 cd m<sup>-2</sup> at 12.8 V and 651 cd m<sup>-2</sup> at 13 V, respectively. The maximum luminescence efficiency of BE-PPV and BD-PPV was in the range of 0.37–0.40 cd  $A^{-1}$ . Using the ITO/PEDOT:PSS/BE-PPV/Ca/Al configuration, the device emitted green–yellow light with a turn-on voltage of  $ca. 4.3$  V.<sup>109</sup> The device of BE-PPV exhibited the maximum luminance of about 157 cd  $m^{-2}$  at 10.5 V. Shu *et al*.<sup>110</sup> have also synthesized other  $poly(p$ -phenylenevinylene) derivatives (PPV-PP) modified by two types of pentaphenylene dendrons, as pendant groups. These dendritic structures can help to increase the solubility of PPV-PP. The double-layer OLED devices were fabricated as ITO/PEDOT/PPV-PP (34)/Mg:Ag/Ag and evaluated. The EL of this device exhibited a green light having CIE color coordinates of (0.30, 0.62). The maximum luminance efficiency was 1.93 cd  $A^{-1}$  at 824 cd m<sup>-2</sup> with a current density 42.6 mA  $cm^{-2}$ . Wei and co-workers<sup>111</sup> have



Fig. 13 Heck coupling was used to prepare this orange–red emitting hyperbranched polymer.

synthesized a high molecular weight fluorescent poly(p-phenylenevinylene) incorporating side-chain-tethered dendritic phenyl groups (DENPPV) through the Gilch route and copolymer of DENPPV with 2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene (MEHPPV). The double-layer EL devices having the configuration ITO/PEDOT:PSS/polymer/Ca/Al were fabricated; whereas, the EL of the copolymer MEHPPV/ **DENPPV** (25 : 75) (0.12  $\text{Im } W^{-1}$ ) was 70% higher than that of MEHPPV  $(0.07 \text{ lm W}^{-1})$  under similar condition.

#### D Hyperbranched polymers

Branched polymers have physical properties distinct from their linear analogues in both solution and the melt. However, the more complicated the structure—the more difficult it is to develop techniques for synthesizing polymers with welldefined molecular architectures; as well, characterization becomes increasingly more problematic. Many synthetic approaches have been presented by mainly polycondensation reactions<sup>25,112,113</sup> for the preparation of hyperbranched polymers. In most cases, the resulting polymers exhibited high molecular and compositional polydispersity, and their molecular architectures could not be precisely defined. Even so, their properties were quite interesting; thus, these polymers can be used in many applications.

Tao et al.<sup>114</sup> synthesized hyperbranched polycarbazole (HBPC), as an ETL, and main chain polymer of poly- [9-tetradecanyl-3,6-(dibutadiynyl)carbazole], as a HTL, for double-layer LEDs. It takes two steps to synthesize HBPC, first esterifying 3,6-diformyl-9-(11-hydroxyundecyl)carbazole with cyanoacetic acid in presence of N,N-dicyclohexylcarbodiimide (DCC), then polycondensation via a Knoevenagel reaction.<sup>115</sup> The device for LED was fabricated as: ITO/HTL/ETL/Al. It possessed a turn-on voltage of ca. 15 V for current and luminescence; its external quantum efficiency is 0.08%. In the case of the single-layer device (ITO/HTL/Al), an apparent current was observed, but it did not show any visible emission. This result implied that the hetero-junction formed by two polymeric layers was able to confine charge and thus bring about efficient electron-hole capture to generate excitons.

Using the Heck coupling reaction $116$  in a one-pot polycondensation, Qin and co-workers<sup>117</sup> synthesized a new orangered light-emitting hyperbranched polymer (36; Fig. 13) using an  $A_2 + A_3$  approach. The EL property of the hyperbranched polymer was studied with a single-layer device (ITO/HBP/Al), a double-layer device (ITO/HBP/Alq3/Al), and a triple-layer device (ITO/PEDOT/HBP/Alq3/Al). The double-layer device showed the highest luminescence, up to 662 cd  $\text{m}^{-2}$  at 7.0 V and a driving voltage of 4.0 V; its external quantum efficiency was  $0.19\%$  at 130.61 mA cm<sup>-2</sup>. The triple-layer device exhibited a modest decrease, with a 14 nm blue-shift of the EL spectra and luminescence of 405 cd  $m^{-2}$  at 8.0 V and a turn-on voltage of 4.5 V. A double-layer device with PEDOT, as the hole-transporting layer, and without Alq3, as the electron transporting layer, showed poor EL performance with a luminescence falling to 65 cd  $m^{-2}$  and 8.0 V and turn-on voltage of 4.5 V. The reason may be derived from insufficient electron injection and consequently hole annihilation by electrons at the cathode.



Fig. 14 Hyperbranched oxadiazole-containing polyfluorenes.

Hyperbranched oxadiazole-containing polyfluorenes (37; Fig. 14) were synthesized by Huang and co-workers<sup>118</sup> using a " $A_2 + A'_2 + B_3$ " approach, based on a Suzuki polycondensation. Three monomers, 2,7-dibromo-9,9-dioctylfluorene, 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) and 2-(4 bromophenyl)-5-(3,5-dibromophenyl)-1,3,4-oxadiazole were used for the hyperbranched polymers. Standard LED devices were fabricated with the configuration of ITO/PEDOT/HBP/Ba/Al and  $ITO/PEDOT/PVK/HBP/Ba/Al$ . In case of  $POF<sub>10</sub>$ , the maximum brightness is 165 cd  $m^{-2}$  at 12 V, while it reaches 1150 cd m<sup>-2</sup> at 14 V after adding PVK layer; the POF<sub>5</sub> construct showed similar results.

Peng et al.<sup>119</sup> prepared a series of hyperbranched, polyfluorenes possessing triarylpyrazoline cores based on the Suzuki  $A_2 + A'_2 + B_3$  coupling protocol. Polymer light emitting diodes with an ITO/PEDOT/polymer-TPBI/Alq3/Mg:Ag device configuration exhibited good EL properties. Under these conditions, polymer 38 emitted pure blue light with a turn-on voltage of 5.3 V and exhibited an EL efficiency of nearly 2%.

He and co-workers<sup>120</sup> have synthesized a series of hyperbranched alternating copolymers by either Suzuki or Grignard coupling condensation between two  $AB_4$ -type tetrahedral monomers [i.e., tetra(4-bromobiphenyl)silane and tetra(2-bromo-9,9 dihexylfluorenyl)silane] with AB<sub>2</sub>-type dibromo or diboronic acid monomers of 9,9-dihexylfluorene or oligothiophene. Among the synthesized hyperbranched polymers, two polymers derived from the 9,9-dihexylfluorenyl)silane-based monomer and 9,9-dihexylfluorene-2,7-diboronic acid and the other derived from the 4-bromobiphenyl)silane-based monomer and 5,5'-dibromo-3,3'-dihexyl-2,2'-bithiphene were selected for use in polymeric electroluminescent diodes. Double-layer devices with a ITO/PEDOT/polymer/LiF/Ca/Ag configuration were also fabricated. In the first case, it emitted a bright blue light starting at about 9.6 V and reaching a brightness of 167 cd  $\text{m}^{-2}$ at a bias of 15.2 V. The obtained maximum current efficiency was 0.78 cd  $A^{-1}$  (at 15.2 V with current density of 21.5 mA cm<sup>-2</sup>). For the second case, the device of emitted visible green light starting at about 5.8 V and reaches a brightness of 17.23 cd  $\text{m}^{-2}$ at a bias of 8.8 V. The maximum current efficiency was measured to be 0.04 cd  $A^{-1}$  (at 8.8 V with current density of 47.14 mA  $\text{cm}^{-2}$ ).

Bai and  $\cos^{-121}$  synthesized a hyperbranched conjugated polymer with 1,3,5-trivinylbenzene, as the core, phenylenevinylene, for conjugation, and dimethylamine benzene, as the termini. The device was fabricated with an ITO/PEDOT/HBP/Ba/Al configuration. The turn-on voltage of the OLED is ca. 9.0 V, the maximum quantum efficiency is ca. 0.02%.

A novel, hyperbranched phthalocyanine was constructed by Lee *et al.*<sup>122</sup> for use as a hole injection layer that is coated on the ITO layer of an OLED. This material was created to replace the more ubiquitous poly(3,4-ethylenedioxythiophene(PEDOT)/polystyrene sulfonate (PSS) coating, currently in use. It was found that this coating increased the luminescence efficiency and device brightness in single layer devices, as well as reduced current leakage, thereby minimizing 'cross-talk' in panel devices.

## **Conclusions**

Observed device performance associated with the use of dendritic molecules has been summarized. Challenges remain using these dendritic molecules to achieve pure red-, greenand blue-light, full-color applications. In particular, the shape, generation, and components of the dendritic materials need to be addressed and optimized to overcome the specific factors that limit device performance. In particular, the use of metal–ligand complexation with various transition metals has revealed advantages for high-efficiency devices due to the phosphorescence effect, which is critical to full-color

applications. Comparison of devices fabricated with dendritic, dendronized, and hyperbranched materials is difficult due to the multitude of potential device configurations and emissive layer functionality, architecture, and combinations. However, it appears in some instances that higher generation materials offer better solutions than those of lower generation. Reasons may include better solubilities leading to better processability, thus resulting in more homogeneous films and layers as well as enhanced interacting functionality. Efforts to evaluate and compare are also precluded by the potential to use these materials in other capacities, such as hole injection layers. Given the rich chemistry available for investigation of these dendritic materials in OLEDs, as well as other electronic devices, and the largely untapped methods available for component construction, such as fiber electrospinning, it is clear that there will be no shortage of work in this area. Since intensive research efforts are ongoing to develop new material designs and device architectures, these advances in the design and engineering of dendritic molecules will open new avenues to flat panel displays and futuristic applications.

## Acknowledgements

Support was provided the Fundamental R&D Program for Core Technology of Materials funded by The Ministry of Commerce, Industry, and Energy, Republic of Korea (S.-H. H) and National Science Foundation (DMR-0705015, CHE-0420897), Air Force Office of Scientific Research (F49620-02-1-0428,02), and Ohio Board of Regents (G. R. N.).

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