Electron Transport Materials for Organic Light-Emitting Diodes

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A comprehensive review of the literature on electron transport materials (ETMs) used to enhance the performance of organic light-emitting diodes (OLEDs) is presented. The structure−property−performance relationships of many classes of ETMs, both small-molecule- and polymer-based, that have been widely used to improve OLED performance through control of charge injection, transport, and recombination are highlighted. The molecular architecture, electronic structure (electron affinity and ionization potential), thin film processing, thermal stability, morphology, and electron mobility of diverse organic ETMs are discussed and related to their effectiveness in improving OLED performance (efficiency, brightness, and drive voltage). Some issues relating to the experimental procedures for the estimation of relevant material properties such as electron affinity and electron mobility are discussed. The design of multifunctional electroluminescent polymers whereby light emission and electron- and hole-transport properties are combined in one material to achieve efficient single-layer OLEDs is also discussed. The review concludes with a brief perspective on the challenges that future research should address.

1. Introduction

The tremendous research effort following the discovery of efficient electroluminescence in organic and conjugated polymer thin films[1,2] has resulted in a vast literature on organic light-emitting diodes (OLEDs).[1−3] Reviews of different aspects of the field of OLEDs have appeared, including electroluminescent materials[4] and device physics and engineering.[5] Evidence of the considerable progress that has been made in the field is that flat-panel displays based on OLEDs are emerging in commercial products such as cell phones and digital cameras.[6] Major challenges remain, however, including the need to significantly improve the performance and durability of blue, green, red, and white OLEDs for displays and lighting.

One of the key challenges on the path to developing the next generation of high-performance OLEDs is the design and synthesis of readily processible and thermally robust emissive and charge transport materials with improved multifunctional properties. OLEDs are double charge injection devices, requiring the simultaneous supply of both electrons and holes to the electroluminescent (EL) material sandwiched between two electrodes (Figure 1). To achieve an efficient OLED with the single-layer configuration shown in Figure 1a, the organic EL material would ideally have a high luminescence quantum yield and be able to facilitate injection and transport of electrons and holes. This demand of multifunctional capabilities from a single organic material is a very difficult one to meet by nearly all current materials. Most highly fluorescent or phosphorescent organic materials of interest in OLEDs tend to have either p-type (hole-transport) or n-type (electron transport) charge transport characteristics.[1−5] A consequence of this is that the simplest OLED configuration shown in Figure 1a, where an organic emitter layer is sandwiched between a transparent anode and a metallic cathode, gives very poor efficiency and brightness.[1−5] The use of two or more different materials to perform the required functions of efficient light emission and good electron- and hole-injection and transport properties in an OLED has resulted in orders of magnitude improvement in device performance, albeit with the attendant more complex OLED architectures shown in Figure 1b−d.[1−5] Interestingly, a similar strategy of multilayered device configurations, allowing the independent optimization of organic materials for charge transport, light absorption, and charge photogeneration in photoreceptors, was instrumental to the successful commercial development of organic electrophotographic imaging for copiers and printers.[7]

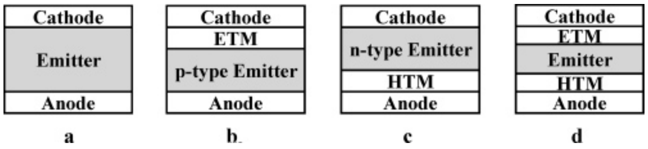

Figure 1. Common OLED architectures with a hole-transport material (HTM) and an electron-transport material (ETM).

The energy-level diagrams in Figure 2 define some of the electronic structure parameters relevant to designing organic materials for OLEDs. In a single-layer OLED (Figure 2a), the electron affinity (EA) or lowest

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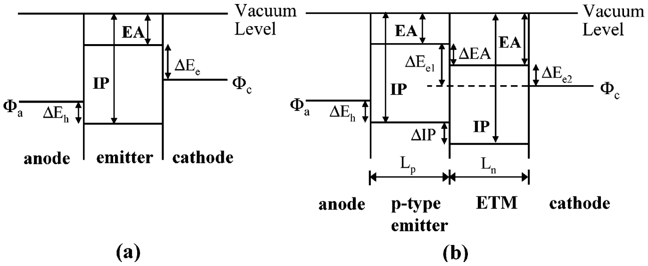
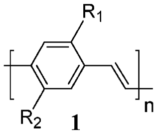


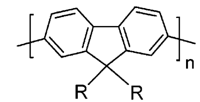
Figure 2. Energy-level diagrams of (a) a single-layer OLED and (b) a two-layer OLED based on a p-type emitter and an ETM.

unoccupied molecular orbital (LUMO) level and the ionization potential (IP) or highest occupied molecular orbital (HOMO) level relative to the cathode work function (Φ_c) and the anode work function (Φ_a), respectively, determine the charge injection into the diode. Large mismatches, thus large barriers for hole injection at the anode ($\Delta E_h = \Phi_a - \mathrm{IP}$) and electron injection at the cathode ($\Delta E_e = \Phi_c - \mathrm{EA}$), lead to poor OLED performance. For the commonly used indium tin oxide (ITO) anode ($\Phi_a = 4.7-4.8$ eV) and air-stable cathodes such as aluminum ($\Phi_c = 4.3$ eV), most emissive organic materials have some barrier for hole injection and a particularly large barrier for electron injection as exemplified by the arylene vinylene polymers **1** and the polyfluorenes **2**.[1-5] Poly(*p*-phenylenevinylene) (PPV, **1a**), with an IP of 5.1 eV and an EA of 2.7 eV, was used to fabricate the first polymer LEDs, ITO/PPV/Al; they had very low external quantum efficiencies (EQEs $\sim 10^{-4}$ to 10^{-3} %).[2] By using calcium cathodes ($\Phi_c \sim 2.9$ eV) substantial improvements in EQE and brightness were realized, confirming the critical role of charge injection barriers in OLEDs.[3] However, the high reactivity of calcium and other low work function metals in air necessitated an alternative and more practical strategy of using separate electron transport materials (ETMs) and hole transport materials (HTMs) to improve and control charge injection and transport in OLEDs.[4,5,8]



1

$R_1 = R_2 = H$, 1a (PPV)
$R_1 = OMe$, $R_2 = OCH_2CH(C_2H_5)(C_4H_9)$, 1b (MEH-PPV)



2

$R = C_8H_{17}$, 2a (PFO)

The introduction of one or more layers of charge transport materials in addition to the emitter layer (Figure 1b–d) provides a powerful means to controlling charge injection, transport, and recombination in OLEDs. The presence of an ETM layer in the two-layer OLED configuration based on a p-type emitter (Figure 2b) not only lowers the barrier for electron injection ($\Delta E_{e2} < \Delta E_{e1}$) but also serves to block holes since the IPs of ETMs are generally large ($\Delta IP > 0$). Since hole mobility (μ_h) is orders of magnitude larger than electron mobility (μ_e) in most emissive organic semiconductors,[9] existence of an ETM layer can dramatically reduce the hole current in the OLED by virtue of the band offset and the greater electron mobility than hole mobility ($\mu_e > \mu_h$) in the ETM.[5] Similarly an HTM layer in combination with an n-type emitter (Figure 1c), such as aluminum quinolate (Alq_3)[1] or polyquinoline,[10a] can significantly improve OLED performance; in this case, the HTM facilitates hole injection and blocks electrons.

In this paper we review the literature on electron transport materials used to control charge injection, transport, and recombination in OLEDs. The molecular architecture, electronic structure (electron affinity and ionization potential), thin film processing, thermal stability, morphology, charge carrier mobility, and OLED applications of diverse organic electron transport materials are discussed in relation to their effectiveness in enhancing OLED performance. We highlight the structure–property–performance relationships of many different classes of electron transport materials used to enhance the performance of small-molecule- and polymer-based OLEDs. Because OLED performance (external quantum efficiency, brightness, luminance yield, turn-on or drive voltage) depends on many extrinsic variables such as film thicknesses of the layers, measures of the effectiveness of ETMs in improving OLED performance are necessarily in relative terms.

Among the important properties an electron transport material should have in order to substantially enhance OLED performance include the following. (i) A reversible electrochemical reduction with a sufficiently high reduction potential; this facilitates electron transport which can be thought of as a series of redox processes within the organic film.[11] (ii) Suitable EA and IP values relative to the p-type emitter, thereby allowing minimization of the barrier for electron injection, reduction of turn-on/operating voltage and effective hole blocking. We note that if the EA is too high (e.g., 4.0 eV) relative to that of the p-type emitter such as **1a** or **1b** (EA ~2.7–3.0 eV), EL can be significantly or even completely quenched due to efficient exciton dissociation.[10] To also serve as an efficient hole blocker, the material should have a wide band gap energy with a high IP value (>6.0 eV) and an EA value closely aligned with that of the p-type emitter. (iii) High electron mobility (μ_e), to move the charge recombination zone away from near the cathode and improve the exciton generation rate. An electron mobility in the ETM comparable to the hole mobility (μ_h) in the p-type emitter would be ideal, however, electron mobilities in organic materials can be several orders of magnitude less than hole mobilities.[9] (iv) High glass transition temperatures (T_g) and thermal stability to withstand inevitable Joule heating encountered during OLED operation, especially at higher electric fields and current densities. (v) Processability to uniform, pinhole-free, thin films either by vacuum evaporation (low molar mass ETM) or by spin casting, printing, and related techniques (soluble polymeric ETM). (vi) Amorphous morphology, which prevents light scattering and crystallization-induced degradation.

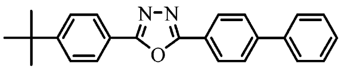
The experimental determination of the absolute electronic energy levels, EA and IP values relative to vacuum, of organic materials including ETMs is difficult.[12] Various experimental methods have been used to estimate these energy levels, including cyclic voltammetry (CV)[12a,b] and photoelectron spectroscopies (UPS and XPS).[12c] The known strong correlation of theoretical electron affinities and experimental redox potentials suggest that, if done carefully, CV can be used to obtain reasonably good estimates of EA and IP values.[12d,e] However, the use of different scaling factors to relate the redox potentials (vs SCE or internal standards such as ferrocene) to vacuum have led to a lot of ambiguity over the reported energy levels. Besides, EA is sometimes estimated as the difference between an IP determined by UPS or XPS and the optical band gap (E_g) of the material. The IP levels estimated from UPS are generally higher than those estimated by CV, making it difficult to compare EA/IP values measured for the same material by different laboratories. We recommend that EA/IP values be estimated from redox data based on the following: EA (eV) = $E_{\mathrm{onset}}^{\mathrm{red}}$ (vs SCE) + 4.4; IP (eV) = E_{onset}^{ox} (vs SCE) + 4.4. This is based on an SCE energy level of 4.4 eV relative to vacuum. We note that the SCE energy level relative to vacuum has sometimes been taken to be 4.8 eV; however, we believe that this leads to physically unrealistic EA/IP values. In this review, therefore, we have tried to compare the EA/IP values of different ETMs based on a common scale of 4.4 eV SCE energy level below vacuum, wherever possible. Regarding the literature EA/IP values quoted in this review, all the CV experiments on small-molecule-based ETMs were done in solution whereas those on polymeric ETMs were performed in thin films, unless otherwise mentioned. We point out that measured redox potentials generally increase by a few tenths of an eV (0.2 eV) in going from solution to thin films. Thus, the EA/IP values derived from CV measurements in solution are still fairly applicable to the discussion of energy levels in thin-film OLEDs.

Electron transport in organic materials remains poorly understood and electron mobility data are relatively scarce compared to hole mobilities.[11] Unlike band-like transport observed in organic single crystals,[11c] electron transport in disordered amorphous organic semiconductors occurs by carrier hopping between spatially localized states. This process can be regarded as a one-electron reduction of a neutral molecule coupled with the oxidation of its anion. This requires the facile formation of very stable anions of the organic semiconductor to prevent trapping of the electron by extrinsic chemical impurities such as molecular oxygen. Since most current organic molecules lack the high solid-state electron affinity (EA) essential to forming such stable anions in the presence of oxygen-containing atmosphere, injected electrons are readily trapped, resulting in dispersive electron transport with low carrier mobilities in the organic semiconductor. The fact that electron mobilities as high as 10 cm^2/Vs have been demonstrated in some organic single crystals[11c] suggests that there is no inherent limitation to achieving high electron mobilities in n-type organic semiconductors. The real challenge is to achieve air-stable electron transport with high mobilities under the more practical ambient conditions. Some of the experimental methods that provide mobility data include time-of-flight (TOF),[11a,b] space-charge-limited-current (SCLC),[11c] drift current method,[11d] and field-effect transistors.[11e,f] We have included available data on the electron mobility of various ETMs, estimated by one of these methods, to allow this factor to be considered in comparing their effectiveness as ETMs in improving the performance of OLEDs.

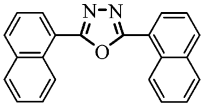
2. Electron Transport Materials in OLEDs

Oxadiazole Molecules and Dendrimers. Oxadiazole molecules and polymers are among the most widely investigated electron transport materials for OLEDs. The oxadiazole molecule 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD, **3**),[13−15] with an EA of 2.16 eV and an IP of 6.06 eV,[15c] was first used as an electron transport material in a bilayer OLED based on a triphenylamine derivative as the emissive material.[13a] The bilayer LEDs using PBD were 10^4 times more efficient than those without PBD, demonstrating the value of a separate electron transport layer in an OLED.[13a] However, the vacuum-evaporated amorphous PBD thin films (T_g ~60 °C) crystallized over time due to joule heating during device operation. This results in reduced device lifetimes.[13b]

To overcome the problem of crystallization, PBD was dispersed in a poly(methyl methacrylate) (PMMA) matrix that can be spin coated. External quantum efficiencies (EQE) of 2−4% were achieved by blending PBD in PPV-based electroluminescent polymers at 20 wt % concentrations.[14] Improvements by factors of 8−10 in EQE of PPV-based LEDs have also been achieved by using a PBD/PMMA blend as the ETM.[15a] Similar to PBD, 2,5-bis(4-naphthyl)-1,3,4-oxadiazole (BND, **4**), with similar electrochemical properties, has also been used as an ETM in LEDs.[15b] Both PBD and BND have shown comparable electron mobilities of ~2 × 10^{-5} cm^2/Vs at high electric fields (~1 × 10^6 V/cm),[16a,b] which explains their effectiveness as ETMs. These relatively high electron mobilities can be attributed to the planar molecular shapes of 2,5-diaryl-1,3,4-oxadiazoles and their stacking behavior with close intermolecular interactions as revealed by X-ray diffraction.[16c] Phase separation in PBD/polymer blend films is one disadvantage of blending small molecules (PBD and BND) with polymers.

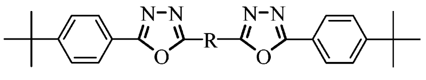


3, PBD

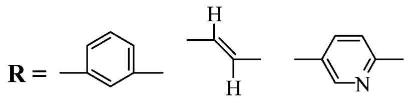


4, BND

Dimeric oxadiazoles **5a**−**c**[17,18] with higher glass transition temperatures have been synthesized and tested as ETMs in an effort to increase the stability of the amorphous films. The presence of the additional oxadiazole ring in these dimeric derivatives leads to a higher EA than that of PBD as demonstrated by **5a** with an EA of ~2.8 eV compared to 2.16 eV for PBD.[17b] LEDs using **5a** as an ETM and a related oxadiazole as the emissive material had a brightness of ~1,100 cd/m^2 and were more stable compared to similar devices using PBD as the ETM.[17a] When **5a** was used as an ETM in conjunction with a PPV derivative as the green emissive layer, a 1% EQE (luminous efficiency of 6 lm/W) was achieved.[17b] Analogues of **5a** have been synthesized and successfully used in MEH−PPV LEDs as ETMs either as blends or bilayers.[18] Using **5c** as the ETM, the bilayer LED was ~30 times more efficient than the single layer MEH−PPV LED.[18] X-ray diffraction data suggested that **5c** was partially crystalline and hence could have a higher electron mobility than **5b**. A slightly higher EA value was observed in **5c** relative to **5b** due to the presence of the pyridine ring.[18]



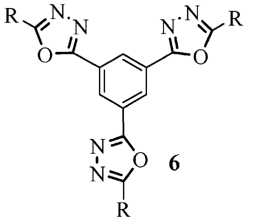
5



5a **5b** **5c**

Branched or starburst oxadiazole molecules[19,20] with higher T_gs (125−222 °C) and improved thermal stability exemplified by **6a**−**c** and **7** have been investigated as ETMs. The starburst molecular architecture enhances the solubility of the molecules presumably by preventing intermolecular stacking. Compounds **6a** and **b** have a high T_g (142 °C for **6b**),[19b] a high EA (3.2 eV), and a high IP (6.5 eV).[19b] Compound **6b** showed an electron drift mobility of 1.2×10^{-6} cm^2/Vs at an electric field of 7×10^5 V/cm.[19b] Using **6a** as an ETM in a multilayer LED, an EQE of 4% with a brightness of 19 000 cd/m^2 was achieved.[19a] Improved electron injection/transport and hole-blocking effect of **6a** explain the much-improved LED performance. Bilayer devices made with a PPV emissive layer and **6b** as the ETM were ~30 times more efficient than single-layer PPV LEDs.[19b] A series of oxadiazole-containing dendrimers with various core and shell groups has been reported.[20] The first generation dendrimer **6c**, containing 9 oxadiazole groups, has a very high T_g of 222 °C.[20b] Although no electrochemical data could be found for compound **6c**, it is likely that its EA would be similar to that of **6b**. Bilayer PPV devices using **6c** as the ETM showed an EQE as high as 0.4%, compared to 0.001% for the single-layer PPV LEDs.[20b]

Along the lines of high T_g materials, several tetraphenylmethane-based oxadiazoles (**7a**−**c**)[21] were developed. Since π-conjugation is limited to one arm of the four-armed compound, the optical and electrochemical properties of **7a**−**c** are very similar to those of PBD, except that **7c** has a slightly higher EA of 2.26 eV due to the peripheral CF$_3$ groups.[21] However, the thermal properties of **7a**−**c** are significantly enhanced compared to those of PBD, with T_g of 97−175 °C and T_d of 405−499 °C. In terms of device performance, the EQE is comparable at ~0.7% when using **7c** or PBD as the ETM and Alq$_3$ as the emissive layer. However, the devices with **7c** are expected to be more stable owing to its superior thermal properties; **7c** crystallizes above 200 °C compared to 70−90 °C for PBD.[21] Since compounds **6** and **7** are soluble in organic solvents, uniform thin films for devices can be made by spin coating, rather than by vacuum evaporation.



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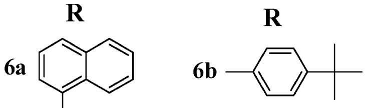
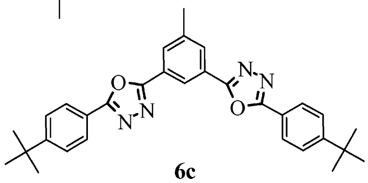
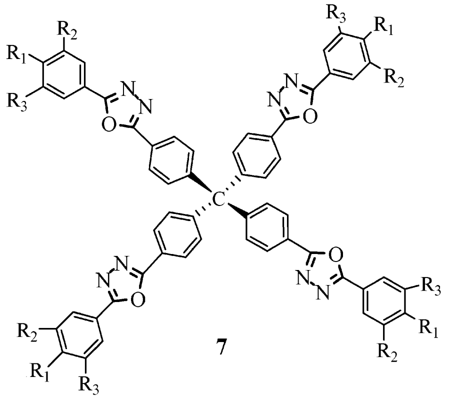




6c

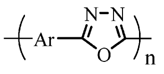


7

	R_1	R_2	R_3
7a	H	C(CH$_3$)$_3$	C(CH$_3$)$_3$
7b	OCH$_3$	OCH$_3$	H
7c	H	CF$_3$	H

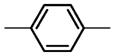
Polymeric Oxadiazoles. Compared to low-molecular-weight oxadiazole compounds, oxadiazole-containing polymers are expected to have higher T_gs and to be less susceptible to crystallization under device operation. They can be readily processed into amorphous thin films by spin coating of solutions. However, most of the earlier aromatic poly(1,3,4-oxadiazoles) (**8a** and **b**) were completely insoluble in organic solvents and could only be processed using strong acids (sulfuric acid or methanesulfonic acid).[22,23] Due to their stiff backbones, these polymers had excellent thermal stability with no distinct T_g, and T_d above 450 °C.[22] Polyoxadiazoles **8a** and **b** showed reversible electrochemical reductions and irreversible oxidations, suggesting that they were easily n-doped.[23a] Polymers **8a** and **b** possessed high EAs of ~2.8−3.6 eV and high IPs of ~6.0 eV, which are appropriate for use of such materials as ETMs in OLEDs. However, due to their insolubility in organic solvents, they have so far not been fully explored as ETMs in LEDs.

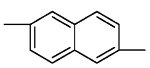
Polyoxadiazole derivatives **9a** and **b** and **10a**−**c**, incorporating tetraphenylsilane[23b] or hexafluoroisopropylidene functional groups[24] in the main chain, were made in efforts to improve solubility in organic solvents. Polymers **9a** and **b** were soluble in organic solvents (chloroform, dimethylacetamide (DMAc), and *N*-methylpyrrolidone (NMP)). Their reduction potentials were similar to those of polymers **8a** and **b**; however, **9a** and **b** were very poor emitters when used in single-layer LEDs (EQE ~10^{-4} %).[23b] Introduction of hexafluoroisopropylidene groups in polymers **10a** and **b** rendered them soluble in solvents (tetrahydrofuran (THF), dimethylformamide (DMF), chlorinated hydrocarbons, DMAc, and 2-butanone).[24a,b] However, **10b** was less soluble than **10a**, whereas **10c** was only soluble in acids (trifluoroacetic acid (TFA)). Electrochemical properties of polymer **10c** revealed a reversible reduction with an EA of ~2.8 eV, suggesting that these polyoxadiazoles could be good ETMs.[24d] Indeed, an increase of about 40-fold in EQE was achieved in bilayer LEDs using MEH−PPV as the emissive material and polymers **10a** and **b** as the ETMs.[24a,b] Using **10c** as the ETM with PPV,

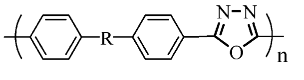


8

Ar

8a 

8b 



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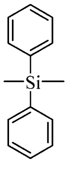
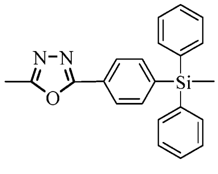
R

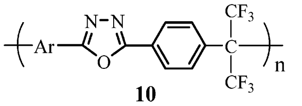


9a

R



9b



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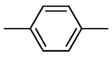
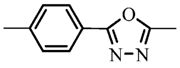
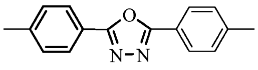
Ar 

10a

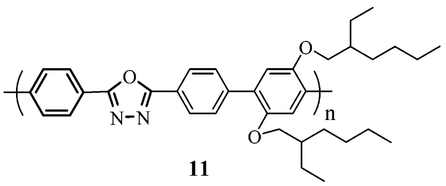


10b



10c

about a 3−10-fold increase in EQE compared to single-layer LEDs was achieved.[24c]



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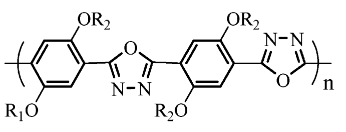

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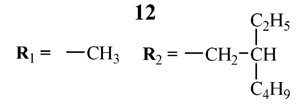
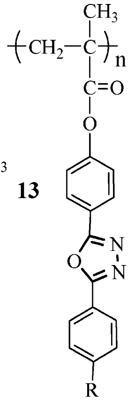


$R_1 = -CH_3 \quad R_2 = -CH_2-CH(C_2H_5)(C_4H_9)$

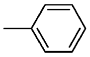
Conjugated polymers containing oxadiazole rings in the main chain and bearing long side groups attached to phenylene moieties, **11** and **12**, were found to be completely soluble in organic solvents.[25] Polymer **11** has a T_g of 196 °C and thermal stability up to 370 °C.[25a] Compared to single layer MEH−PPV LEDs, the bilayer LEDs using polymer **11** as an ETM showed an improvement in brightness and EQE by factors of ~50 and 25, respectively. Polymer **12** had an EA of 2.75 eV and an IP of 5.91 eV,[25b] suggesting good hole blocking when used with PPVs due to a band offset (ΔIP) of ~0.8 eV.



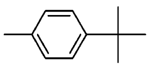
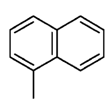
13

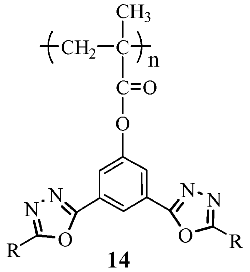
R

13a $-C(CH_3)_3$

13b 

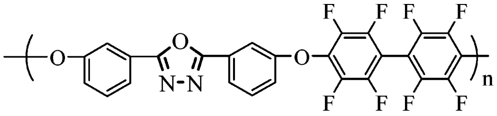
13c H

		
14a	100	0
14b	0	100
14c	25	75

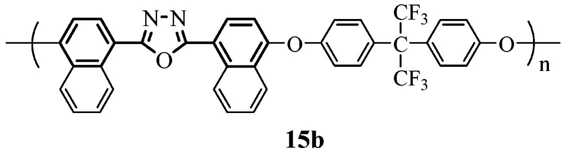


14

Incorporation of oxadiazole moieties either as pendant groups on poly(methyl methacrylate) (PMMA) (**13a**−**c**, **14a**−**c**) or in the backbone of polyaryl ethers (**15a** and **b**) has been widely explored.[26,27] These polymers have higher T_gs relative to PBD or PMMA (T_g ~105 °C). Polymers **13a**−**c** had T_gs ranging from 153 to 169 °C,[26a,27a] whereas polymers **14a**−**c** had higher T_gs of 198−209 °C due to the increased bulkiness of the pendant group with two oxadiazole moieties.[26b] The polymers were soluble in organic solvents (chloroform, toluene, and THF) and were easily processible by spin coating. In bilayer LEDs with PPV, improvement in device efficiency by a factor of 4 was achieved by using **13a**−**c**.[26a,27a] However, OLEDs using polymers **13a**−**c** were found to be unstable, undergoing fast degradation under device operating conditions, and **13a**−**c** were thus deemed not to be promising for LED applications.[27a] The device stability was much improved when using polymers **14a**−**c** in bilayer LEDs with PPV. Device operational lifetimes of ~30 h were achieved using **14a** with device testing in ambient conditions, whereas the corresponding PBD device failed within minutes.[26b] This stability could be a result of the ~40 °C higher T_gs of **14** compared to **13**. It was shown from systematic studies that polymers such as **13c** or polyaryl ethers such as **15a** with high T_gs increased device lifetime, demonstrating a 30-fold improvement in stability.[27a,b] Bilayer LEDs with PPV using such materials as ETMs did not show any change in performance after several months of storage in an Ar-filled drybox. Similarly, polymer **15b** (T_g ~220 °C) was shown to be a very stable ETM for PPV-based LEDs, achieving operating lifetimes of 150 h under ambient conditions without encapsulation.[27b]



15a

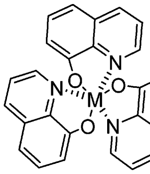


15b

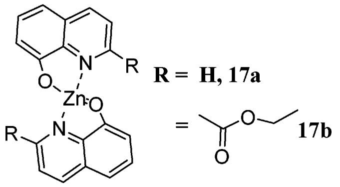
A comparison of polymers containing oxadiazole moieties in the main chain (**10** and **11**) as ETMs in bilayer LEDs to those with oxadiazole groups as pendant units (**13** and **14**) shows that the former are more effective in improving the device performance. Possible reasons for this could be the relatively higher EAs, the higher electron mobilities, and the higher thermal stability in the main chain polyoxadiazoles. On the other hand, a comparison of the overall performance of OLEDs based on low-molecular-weight oxadiazoles and polymeric oxadiazoles as ETMs shows that evaporated small molecules are more effective. A combination of factors such as better chemical purity of the low-molar-mass oxadiazole molecules, ability to form uniform pinhole-free thin films by thermal evaporation, and better electron injection and transport properties can explain the superior performance of evaporated thin films. Clearly, further improvements in the solution processing of polymer-based ETMs is necessary to fully realize their potential for developing next generation high-efficiency and durable OLEDs.

Metal Chelates. Since the pioneering work of Tang and van Slyke in 1987 demonstrating efficient electroluminescence from thin films of tris(8-hydroxyquinoline) aluminum (**16a**, Alq_3),[1a] metal chelates have been intensely explored for OLED applications as emissive and electron transport materials and as host materials for fluorescent dyes.[28,29,35−37] Alq_3 remains the most widely studied metal chelate owing to its superior properties such as high EA (~3.0 eV)[29c,30] and IP (~5.95 eV),[30] good thermal stability (T_g ~172 °C),[32] and ready deposition of pinhole-free thin films by vacuum evaporation.[28] Four polymorphic phases were identified in single crystals of Alq_3 by X-ray diffraction. However, vapor-deposited films were completely amorphous due to the intrinsic polymorphism of Alq_3, likely containing a mixture of both *mer* and *fac* isomers.[31] Close interligand spacings of 3.5−3.9 Å between the hydroxyquinoline ligands lead to electron mobilities of the order of 1×10^{-5} cm²/Vs at electric fields of $0.39-1.3 \times 10^{6}$ V/cm.[33a] Dispersive electron transport in as-received Alq_3 sample changed to a nondispersive mode after careful sample purification by train sublimation, highlighting the importance of impurities as extrinsic charge traps.[33b] However, exposure of the purified Alq_3 films to ambient atmosphere resulted in highly dispersive electron transport, suggesting oxygen-induced trap formation in the films. All these characteristics of Alq_3 explain its effectiveness as an ETM in OLEDs, as demonstrated by the 2 orders of magnitude improvement in EQE of MEH−PPV bilayer OLEDs compared to single-layer LEDs without an ETM.[29b]

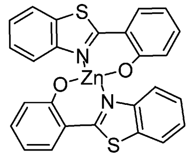
Other metal chelates containing two or three ligands (**16b** and **c**, **17a** and **b**, and **18**) have also been investigated as emissive ETMs in OLEDs.[35−37] Alq_3 has a solid-state fluorescence quantum efficiency of ~25−32%.[34] However, the fluorescence efficiency of Gaq_3 (**16b**) and Inq_3 (**16c**) decreased substantially by nearly a factor of 4.[35b] As emissive materials in OLEDs, the brightness decreased from 11 050 cd/m² for Alq_3 to 6483 cd/m² for Inq_3.[35a] However, Inq_3 was superior to Alq_3 when used solely as an ETM; this is probably due to the higher EA (~3.4 eV) of Inq_3 and higher electron mobility with increase in size of the central metal ion. The subtle differences between the orbital overlaps and atomic interactions in Alq_3 and Inq_3 as evidenced by their crystal structures could explain the differential charge transport properties of their thin films. Metal chelates of substituted 8-hydroxyquinoline and Group II metal ions such as Be^{2+} and Zn^{2+} have also been used in OLEDs.[28,36,37] Yellow-emitting Znq_2 (**17a**) gave a higher brightness (16 200 cd/m²) compared to green-emitting Alq_3.[36a] X-ray diffraction studies on **17a** revealed that the tetramer of **17a** was the energetically favored configuration in vacuum-deposited thin films, unlike in Alq_3 where weak molecular interactions prevent oligomer formation.[36b] Compared to Alq_3 devices, lower operating voltages were obtained with **17a** as an ETM, suggesting enhanced electron injection and transport in **17a**. The stronger π−π overlap between the ligands and the extended electronic states in its tetrameric form may explain these results.[36b] Higher electron mobilities compared to Alq_3 were also postulated for compounds **17b** and **18**, when used as ETMs in OLEDs.[36b,37] Dimers of **18** were identified in vacuum-deposited amorphous films with a close intermolecular π−π interaction of 3.7653 Å, suggesting good potential for charge transport.[37] Although the EA of Alq_3 is higher by ~0.2 eV, apparently improved electron transport in **18** leads to a higher device efficiency (1.96 cd/A) when using **18** as an ETM, compared to devices without **18** (1.1 cd/A).[37] Further improvements in the performance of OLEDs from metal chelates can be achieved through careful ligand and metal substitution.



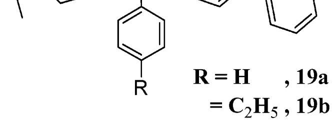
16a-c, Mq_3
a M = Al
b M = Ga
c M = In



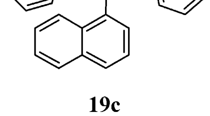
R = H, 17a
17b



18



R = H , 19a
= C_2H_5 , 19b

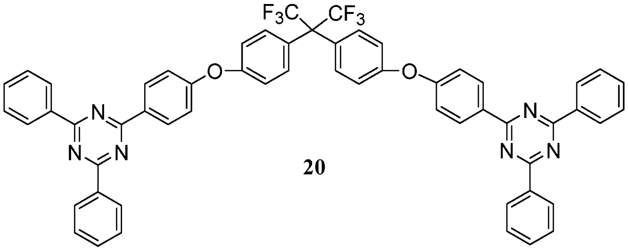


19c

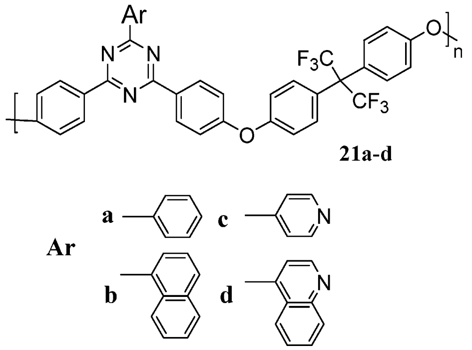
Azole-Based Materials. Triazole, imidazole, oxazole, thiazole, and thiadiazole derivatives constitute a class of azole-based materials that have been used as ETMs in OLEDs. 1,2,4-Triazole compound **19a** was first demonstrated as an ETM in 1993 in multilayer OLEDs fabricated by vacuum evaporation.[38a] OLEDs using **19a** as the ETM with an Alq$_3$ emissive layer had a brightness of 5800 cd/m^2, which was lower than that in devices without **19a** ($\sim$10 000 cd/m^2).[38a] Cyclic voltammetry revealed reversible reductions of the triazoles with EA values ($\sim$2.3 eV) intermediate between oxadiazoles (2.16 eV) and triazines ($\sim$2.5–2.8 eV).[38b] Besides its use as an ETM, **19a** has been demonstrated as a more effective hole blocker than PBD. Bright blue EL from PVK was obtained by using **19a** as an exciton-blocking/electron-transport layer in a multilayer OLED with Alq$_3$ as the electron injection layer.[39] Similarly, by spatial control of the recombination zone in a multilayer OLED, white light with a brightness of 2200 cd/m^2 was achieved by use of a hole-blocking layer **19b**.[40] When a phosphorescent Ir molecule was doped into various ETMs, higher EQEs of 9.7% (at 10 mA/cm^2; Mg:Ag cathode) were obtained using **19c** compared to **5a** or bathocuproine as the host materials.[41] There are only few reports on polymeric analogues of **19**.[27a] For example, poly(triazole ether)s were soluble in organic solvents and had relatively high T_g (125–186 °C). However, no significant improvements in device efficiencies were observed when they were used as ETMs with PPV-based LEDs.[27a]

Triazines. 1,3,5-Triazines have higher EA values than 1,3,4-oxadiazoles (PBD) and 1,2,4-triazoles.[38b] They have thus been explored as building blocks for ETMs for OLEDs. 1,3,5-Triazine ether **20** was used as an ETM for Alq$_3$-based OLEDs.[42a] Amorphous films of **20** with a T_g of 115 °C were obtained by vapor deposition. Cyclic voltammetry of **20** revealed a reversible reduction with an EA of 2.48 eV.[42a] Using **20** as an ETM in OLEDs, EL from Alq$_3$ was achieved with a brightness of $\sim$1000 cd/m^2 and modest improvement in device efficiency by factors of 2–3 was seen. However, triazines such as **20** were found to be inferior ETMs compared to Alq$_3$. Poly(1,3,5-triazine ether)s **21a–d** were amorphous with good thermal stability (T_g = 186–247 °C).[42b] The polymers were sufficiently soluble in organic solvents (THF, NMP, and cyclohexanone) to spin coat thin films. Electrochemistry of model triazines showed EA of 2.47–2.86 eV and IP of $\sim$6.16 eV,[42b] suggesting that polymers **21a–d** have good hole-blocking properties. Using **21d** as the ETM, a bilayer PPV LED had a brightness of 50 cd/m^2 at 22 V, compared to $\sim$1 cd/m^2 for the single-layer PPV LED.[42b] The overall poor performance of the triazines as ETMs for OLEDs despite their high EA suggests that they probably have rather poor electron mobilities.

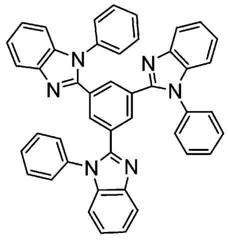
TPBI. The dendritic molecule 1,3,5-tris(*N*-phenylbenzimidizol-2-yl)benzene (**22**, TPBI)[43] has been used both as a host material and as an ETM for OLEDs based on fluorescent[29c,44] and phosphorescent emitters.[29d,45] Compared to Alq$_3$, TPBI has a lower EA (2.7 eV) and a higher IP (6.2–6.7 eV).[44b,45a] Unlike Alq$_3$, TPBI can act as a host or ETM for blue emitters due to its higher optical band gap.[44a,b] Bright blue emission (11 000 cd/m^2) was achieved from a phenylene vinylene oligomer emitter while using TPBI as the electron-transporting host. Additionally, TPBI showed better hole blocking than Alq$_3$ due to its higher IP.[44b] Using TPBI as the ETM in an OLED based on blends of a phosphorescent Ir complex, 10.4% EQE was obtained at much lower voltages compared to those without TPBI.[45a] As a hole blocker, TPBI was shown to be more effective than bathocuproine (BCP), giving more stable OLEDs with repeatable operation. The TPBI diodes gave higher device efficiencies (55 cd/A) compared with BCP ($\sim$25 cd/A).[45b]



20



21a-d



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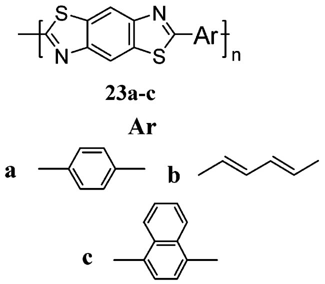
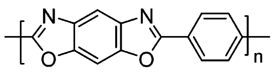


23a-c



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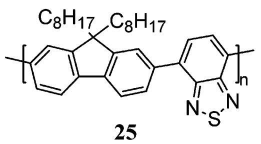
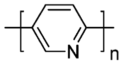


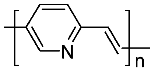
25

Polybenzobisazoles. Polybenzobisthiazoles (**23a–c**)[46a–c] and polybenzobisoxazoles (**24**)[46d–f,47a] are rodlike aromatic heterocyclic polymers with outstanding mechanical properties and excellent thermal stability, with no softening (T_g > 400 °C) before their decomposition at high temperatures above 600 °C in air. The origin of these properties can be traced to the high degree of intermolecular $\pi-\pi$ interactions in the planar molecules in the solid state.[46f,47b] Polymers **23** and **24** have poor fluorescence quantum yields as thin films due to efficient excimer formation.[47b] They are only soluble in strong acids (methanesulfonic acid and chlorosulfonic acid) or Lewis acid/nitromethane from which thin films can be spin-coated.[47c] Fiber X-ray diffraction studies of **23a** (PBZT)[47d] and **24** (PBO)[47e] and computational modeling of oligomers of **23a** revealed torsional angles of 20.5° and 25.7° between the benzobisthiazole and phenyl rings with interchain spacings of 3.3–3.58 Å, indicating the close-packed ordering of the polymer chains. A field effect electron mobility of $\sim 2 \times 10^{-7}$ cm^2/

Vs in **23a** was reported recently.[48a] These polymers possess excellent reversible n-doping characteristics with EA of 2.4−3.0 eV depending on the arylene linkage.[46c,48b] Polymers **23a**−**c** and **24** were used as ETMs in bilayer OLEDs with PPV and MEH−PPV.[48b] With **23a** as the ETM, the bilayer MEH−PPV LEDs had a low turn-on voltage (2.8 V), high brightness (1400 cd/m^2), and ∼2.5% EQE, representing factor of 8−10 improvements compared to the single-layer MEH−PPV LED. Among the polymers investigated, **23a** was the best ETM probably due to the combination of high electron mobility and favorable LUMO level for charge injection.[48b] The polybenzobisazoles seem to be better ETMs for arylene vinylene-based LEDs compared to the previously discussed oxadiazoles, triazoles, and triazines.



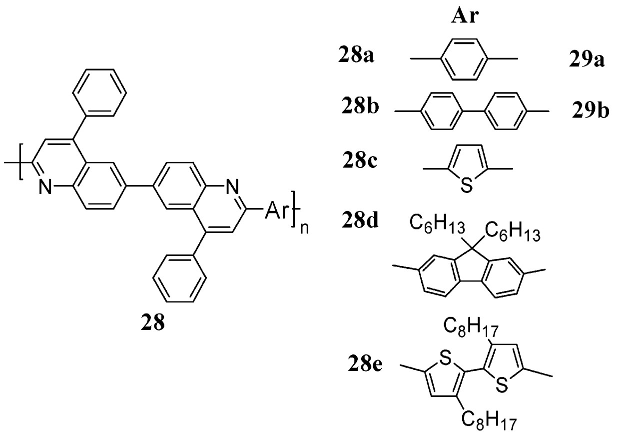
26, PPy



27, PPyV

Benzothiadiazole Polymers. The benzothiadiazole ring is a useful n-type building block for designing ETMs for OLEDs. Poly(2,1,3-benzothiadiazole-4,7-diyl) showed reversible electrochemical reduction in accord with the electron deficient nature of the benzothiadiazole ring.[49a] However, it was not explored as an ETM for OLEDs due to its poor solubility in DMSO and formic acid. Soluble copolymers of benzothiadiazole with fluorescent moieties such as carbazole and fluorene have been synthesized.[49b−d] One promising derivative is the alternating copolymer with 9,9-dioctylfluorene **25** that has an EA of 3.2−3.5 eV and IP of 5.9 eV.[50a,d] Highly dispersive electron transport was reported in **25** with mobility of order of 10^{-3} cm^2/Vs at 5×10^5 V/cm.[50a] High-efficiency OLEDs have been made using **25** as the green-emitting material. Bilayer OLEDs with a fluorene−triphenylamine copolymer as the HTL and **25** as the emissive ETM showed high brightness (∼10 000 cd/m^2) and efficiency (∼14.5 cd/A).[50b] Even higher brightness (153 000 cd/m^2) was achieved in very-small-area (50 μm diameter) OLEDs based on blends of **25** with PFO.[50c]

Pyridine-Based Materials. Polypyridines (PPy, **26**)[51a−c,52a−b] and poly(pyridine vinylene)s (PPyV, **27**)[51d] have been explored as ETMs in OLEDs. Due to the electron-deficient pyridine ring, both polymers have reversible n-doping properties.[51a] Varying EA values of ∼2.9−3.5 eV and IPs of ∼5.7−6.3 eV for **26**,[51a−b] and even higher EA (4.3 eV) and IP (6.7 eV) values for polymer **27**,[51d] have been reported. The EA value of **27** is unrealistically very high since it is estimated as the difference between IP (from UPS) and optical band gap and not from cyclic voltammetry.[51d] The stiff polymer backbones and strong intermolecular interactions in **26** and **27**, similar to the rigid-rod polybenzobisazoles, resulted in ready excimer formation in thin films.[51b] Blue-green EL (∼500 nm) from **26**[51b−c] and yellow-orange EL (585 nm) from **27**[51d] with very low efficiencies were obtained from single-layer OLEDs fabricated by spin-coating polymer films from formic acid solutions. Using **26** as an ETM for PPV OLEDs, enhancements in device efficiencies by factors of 17−60 were obtained compared to the single-layer PPV devices. EL from PPV with a brightness of ∼900 cd/m^2 and EQE of 0.25% was achieved;[52a] better performance was achieved with the polybenzobisazoles (**23a** and **24**) despite their lower EA values.[48b] Organic solvent soluble pyridine-containing copolymers with arylene vinylenes were fairly emissive with enhanced electron-transport properties and were used to achieve voltage-tunable EL colors.[53]



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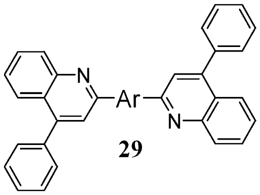
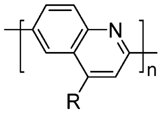


29

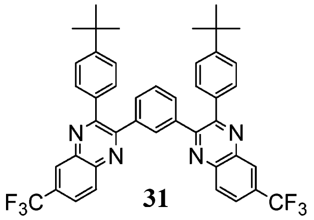


30

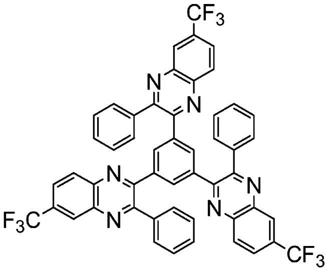
R = C_4H_9 **30a**
= C_6H_{13} **30b**
= C_8H_{17} **30c**
= $C_{10}H_{21}$ **30d**
= $C_{13}H_{27}$ **30e**
= C_6H_5 **30f**

Quinoline-Based Materials. Quinoline, an electron-deficient molecule with a half-wave reduction potential of −2.13 eV (vs SCE),[54] has been widely used as a building block for ETMs for OLEDs. Polyquinolines possess excellent mechanical properties and good thermal stability.[55] Typically, polyquinolines have a T_g above 200 °C and onset thermal decomposition above 400 °C.[55] The poly(phenylquinoline)s (**28a**−**c** and **30f**) are completely soluble in formic acid, allowing thin film processing by spin-coating.[55b−c] Fiber X-ray diffractions of polymer **28b** revealed strong $\pi-\pi$ interchain interactions with nearly coplanar sheets.[56a] Single-crystal structures of related oligomers **29a** and **b** showed close packing with intermolecular spacings of 3.6−4.0 Å and small torsional angles of 13−26° between the central phenyl rings and quinoline moieties.[56b] Cyclic voltammetry on these polyquinolines showed excellent electron-accepting properties with EA of ∼2.4−2.65 eV, depending on the arylene linkage.[12a] Polymers **28a**−**c** and **30f** were used as both ETMs[10a,57a] and emissive materials[57b,c] in OLEDs. In bilayer PPV-based OLEDs, enhancement in EQE by a factor of 100 with brightness of 820 cd/m^2 was seen using **28b** as the ETM with aluminum electrodes.[10a] A brightness of ∼280 cd/m^2 was achieved when **28b** was used as an emissive material in bilayer[57b] or blend[57c] OLEDs. Oligoquinolines such as **29a** and **b** have not been reported as ETMs in OLEDs.

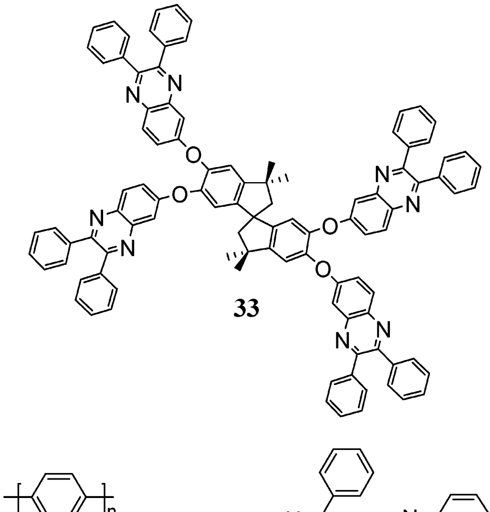
Organic-solvent-soluble polyquinolines,[58] copolymers of phenylquinoline with moieties such as dialkylbithiophenes (**28e**)[58a−c] or dialkyfluorenes (**28d**),[58d−e] were synthesized and used as emissive materials or ETMs in OLEDs. Polymer **28e** showed reversible reduction (EA = 3.0 eV) and was soluble in organic solvents (chloroform and THF).[58a] Solubility of **28e** in formic acid allowed fabrication of bilayer LEDs with MEH−PPV. A factor of 34 enhancement in EQE and high brightness of (∼2300 cd/m^2) were seen with **28e** as the ETM.[58a] Blend OLEDs using **28e** as the emissive ETM in a blend with MEH−PPV gave voltage-tunable EL colors from orange-red to green,[58b] highlighting the flexibility of **28e** as ETMs. Using **28d** (T_g = 214 °C, EA ∼3.2 eV)[58d−e] as an ETM in MEH−PPV-based OLEDs led to improvements in brightness and EQE by factors of 86 and 35, respectively. Regioregular head-to-tail poly(4-alkylquinoline)s **30a**−**e** with good solubility in organic solvents (chloroform and THF) and formic acid were reported.[59a−b] The EA values of **30a**−**e** were ∼2.6 eV, comparable to those of **28a**−**c**. The regioregularity led to self-organized lamellar structures in solution-cast thin films with linear correlation of the interlayer *d*-spacing to the alkyl chain length,[59a−b] suggesting higher electron mobilities than the poly(phenylquinoline)s. When used as the ETMs in bilayer MEH−PPV-based OLEDs, an EQE of up to 3.0% and a brightness of up to 700 cd/m^2 were obtained.[59b]

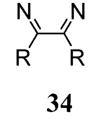


31



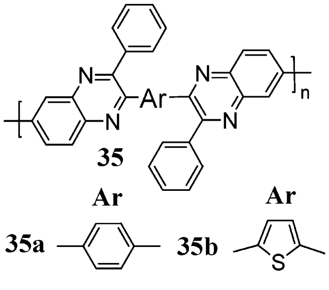
32





34

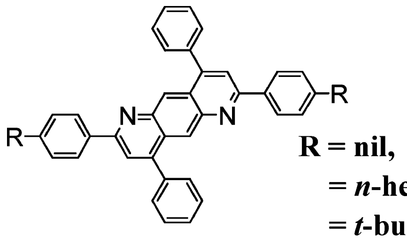
R = H, 34a
= biphenyl, 34b



Quinoxaline-Based Materials. Quinoxaline has a higher EA relative to quinoline due to an additional imine nitrogen in the ring,[54,60] suggesting possible better electron injection and transport properties while retaining the attractive thermal and environmental stability of quinoline-based materials. Bis(phenylquinoxaline) (**31**, BPQ)[61a] and starburst tris(phenylquinoxaline) (**32**, TPQ)[20b,61] were developed for application as ETMs in OLEDs. BPQ, TPQ, and their derivatives had T_gs of 95−139 °C and 147−195 °C,[61a] respectively, and amorphous thin films could be made either by spin coating from organic solvents or by vapor deposition. Compared to quinolines, higher EAs (∼2.56−2.76 eV) and IPs (∼5.76−5.96 eV) were observed for BPQ and TPQ derivatives.[61a] Vapor-deposited films of **32** showed nondispersive electron transport with a mobility of ∼10^{-4} cm^2/Vs (at ∼10^6 V/cm),[61b] which is over 2 orders of magnitude higher than that found in starburst oxadiazole **6b**. Use of BPQs and TPQs as ETMs in PPV-based OLEDs showed a ∼5-fold enhancement in brightness compared to single-layer devices, with EQEs of ∼0.01 to 0.11%.[61a] Amorphous spiroquinoxaline **33** (T_g = 155 °C)[62] was also used as the ETM layer in poly(phenylene ethynylene)-based OLEDs. Although **33** had a comparable EA (2.56 eV) to the BPQs/TPQs, its higher IP (∼6.26 eV) suggested better hole-blocking properties. Using **33** as the ETM resulted in a 65-fold increase in brightness from 4 to 260 cd/m^2.[62]

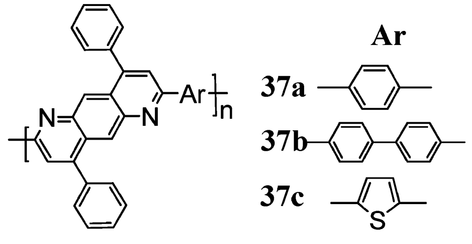
Polyquinoxalines (**34a** and **b**, **35a** and **b**)[60,63] possess excellent electrochemical reduction with EAs (∼3.0−3.3 eV) higher than the polyquinolines (**28a**−**d**). They have excellent thermal stability (T_g > 300 °C) and are soluble in formic acid from which thin films can be spin coated.[60,63] Polymers **34b**[63a] and **35a**[63c] are also soluble in organic solvents (chloroform), affording spin-coating of uniform thin films. A modest 2-fold increase in EL efficiency of PPV-based OLEDs was observed when **34b** was used as the ETM.[63a] A 10-fold increase in EQE (0.35%) was shown by **35a** as an ETM in a similar PPV OLED with a brightness of ∼250 cd/m^2.[63b] Polymer **35b** (EA = 3.0 eV, IP = 5.4 eV) was the best ETM for PPV-based OLEDs giving an EQE of 0.4% and a brightness of over 700 cd/m^2, a 40-fold enhancement over the single-layer diodes.[63c] Thus, polyquinoxalines such as **35b** are better ETMs for PPV-based LEDs than polypyridines[52] and some polyquinolines.[10a]

Anthrazoline-Based Materials. The polycyclic-ring anthrazolines offer the possibility for higher EA and higher electron mobility than the quinolines or quinoxalines owing to their more rigid and planar structure. Several diphenylanthrazolines, **36a**−**d**, were synthesized and successfully used as ETMs in MEH−PPV-based OLEDs.[64] They had excellent thermal stability with T_g and T_d above 300 and 400 °C, respectively. Molecules **36b**−**d** were soluble in chloroform, toluene, and formic acid; amorphous thin films were thus obtained by spin-coating or vapor deposition. X-ray single-crystal structures of **36b**−**d** indicated efficient π-stacking in the solid state with intermolecular spacings of 3.4−3.9 Å.[64] High EAs (∼2.9−3.1 eV) and IPs (∼5.65−5.85 eV) were obtained from cyclic voltammetry, suggesting good electron-transporting/hole-blocking properties in OLEDs. When used as ETMs with MEH−PPV-based OLEDs, up to 50-fold improvement in brightness was seen with EQE as high as 3.1%.[64] These results suggest that the diphenylanthrazolines are superior ETMs for MEH−PPV LEDs compared to Alq$_3$ and oxadiazoles. On the other hand, spin coated polyanthrazolines **37a**−**c**, with comparable EAs (~2.85 eV), gave only marginal improvements as ETMs in PPV-based LEDs.[10a] The probable higher electron mobilities in the uniform amorphous films of diphenylanthrazolines **36a**−**d** combined with their higher IPs could explain their superior performance as ETMs compared to polymers **37a**−**c**.

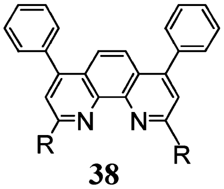


R = nil, 36a
= *n*-hexyl, 36b
= *t*-butyl, 36c
= OCH$_3$, 36d

36



37

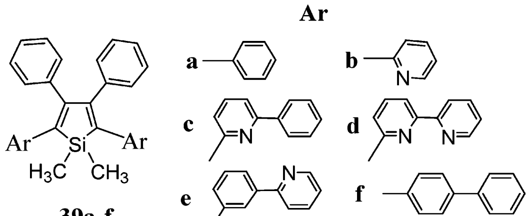


38

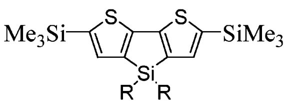
R = H, 38a
= CH$_3$, 38b

Phenanthrolines. Low-molar-mass 1,10-phenanthrolines (**38a** and **b**)[65−68] have been primarily used as exciton/hole-blocking layers in OLEDs owing to their deep HOMO levels (IPs ~6.5−6.7 eV).[65,68b] Their rigid planar structures afford high electron mobilities (5.2 × 10^{-4} cm^2/Vs in **38a** at 5.5 × 10^5 V/cm)[66] and high EA (~3.2 eV for **38b**).[65,68b] Amorphous films obtained by vapor deposition tend to degrade under device operation due to a low T_g (62 °C for **38a**),[67] thus reducing device stability. Thin layers (8 nm) of **38b** between an emissive phosphorescent layer and Alq$_3$ as the ETM gave an improvement in EQE from 4% to 5.6% compared to devices without **38b**.[68a] This is due to the superior hole-blocking properties of **38b** relative to Alq$_3$.

Siloles. The silicon-containing silole ring has a particularly low-lying LUMO level compared to nitrogen-containing heterocycles (oxadiazoles, triazoles, oxazoles, and pyridines) due to its unique electronic structure in which the LUMO level arises from the mixing of the σ^* orbital of the silicon atom and the π^* orbital of the butadiene moiety in the ring.[69,70] 2,5-Diarylsiloles **39a**−**f** were first proposed as ETMs for OLEDs in 1996[69] and various other silole derivatives (**40a** and **b**, **41a**−**c**) have also since been developed.[70−74] Fast, nondispersive electron transport (μ_e ~2 × 10^{-4} cm^2/Vs at 6.4 × 10^5 V/cm)[71a] was observed in vapor-deposited films of **39d** in air, suggesting minimal trapping even in the presence of oxygen. The electron mobility of **39d** was about 2 orders of magnitude higher than that in Alq$_3$ which showed dispersive electron transport due to oxygen-induced traps.[33b,71a] Compared to Alq$_3$, **39d** had a slightly higher EA (3.3 eV),[71b] in part explaining its superior electron transport properties. However, electrochemical investigations revealed irreversible oxidations and reductions for most silole derivatives.[72a,74b] Improved EL efficiencies (1.9 to 2.6 lm/W) were obtained when a layer of **39b**[69] or **39d**[71b] was inserted between the LiF/Al cathode and an Alq$_3$ emissive layer. However, **39b** exhibited poor film stability with crystallization under device operation due to its low T_m (175 °C) and low T_g.[69,73a] Improvement in T_g (up to 81 °C) was achieved via biaryl substitution in **39c**−**e**.[73a] Although the T_gs of **39c**−**e** are lower than that of Alq$_3$, longer device lifetimes in air were seen using **39d** as the ETM, probably due to its superior stability under ambient conditions. Besides their use as ETMs, siloles (**39a** and **f**) are also being explored as emissive materials for OLEDs.[72b,73b−c] Efficient EL from an exciplex of **39f** with a diamine derivative was demonstrated with high brightness (7325 cd/m^2) and maximum EQE of 3.4%, using **39d** as the ETM.[73b]

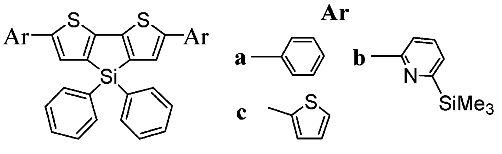


39a-f



R = Ph, 40a
= p-tolyl, 40b

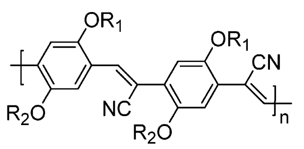
40



41a-c

Vapor-deposited uniform thin films of dithienosiloles (**40a** and **b**, **41a**−**c**) were explored as ETMs.[74] Although no electrochemical redox data were found, EA comparable to Alq$_3$ (~3.1 eV) has been reported for **40a**.[74a] When **40a** and **b** were used as ETMs, the device performance degraded at high applied voltages due to melting or crystallization (T_m ~160 °C for **40a**) of the ETM.[74a,b] Compared to **40a** and **b**, a higher luminance of 16 000 cd/m^2 was achieved using **41b** as the ETM in Alq$_3$-based OLEDs, probably due to the better thermal stability of **41b** (T_m = 295 °C).[74c] Although very promising as ETMs, especially for Alq$_3$-based OLEDs, the thermal stability of these silole-based materials needs to be improved further in order to fully realize their potential.

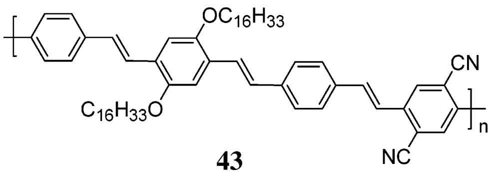
Silole homopolymers such as poly(2,5-silole)s[75a] and poly(1,1-silole)s[75b,c] have recently been reported. They are soluble in organic solvents (chloroform and THF), allowing spin coating of thin films. However, they had very low molecular weights with a low degree of polymerization (~13−20).[75] Although initial EL results from single-layer LEDs have been reported,[75c] they have not been explored so far as ETMs in OLEDs.



42

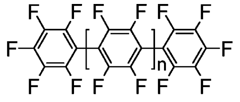
a $R_1 = R_2 = C_6H_{13}$ **42a**

b $R_1 = CH_2CH(C_2H_5)C_4H_9$
$R_2 = CH_3$ **42b**

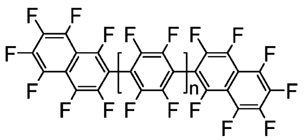


43

Cyano-Containing Polymers. Poly(cyanoterephthalydine)s (**42a** and **b** and **43**) are PPV derivatives with better n-type characteristics than the parent PPV due to the presence of the cyano groups.[76−79] They are soluble in organic solvents, show reversible reductions with typical EAs ~3.0 eV[24d,77b] which is higher than that of PPV (2.7 eV),[10a] and are low band gap polymers (E_g ~2.1 eV) with red[76,77] or near-infrared[78a] luminescence. They typically have low molecular weights[77b,78b] and relatively low T_gs.[79] They have been used as red-emitting materials in polymer LEDs; however, EL efficiencies are generally low.[78] Their small band gaps make their use as ETMs with p-type emissive materials rather difficult due to the strong possibility of efficient energy transfer, causing emission from the CN−PPVs rather than the p-type emitters. Thus, despite their high EAs, their use as ETMs in OLEDs has not been reported. Red EL from **42a** with high internal quantum efficiency (4%) was first reported in 1993 in bilayer OLEDs with air-stable Al cathode and PPV as the HTL.[76a] Efficient red EL from polymer **43** has been reported with a brightness of 3000 cd/m² at 20 V using PPV as the HTL.[79] However, the very low T_g of **43** (~ 45 °C)[79] might lead to accelerated device degradation.

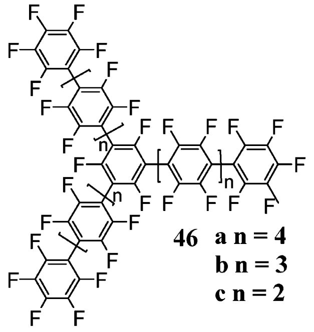


44
a n = 3
b n = 4
c n = 5
d n = 6

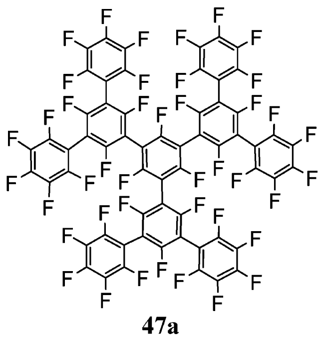


45

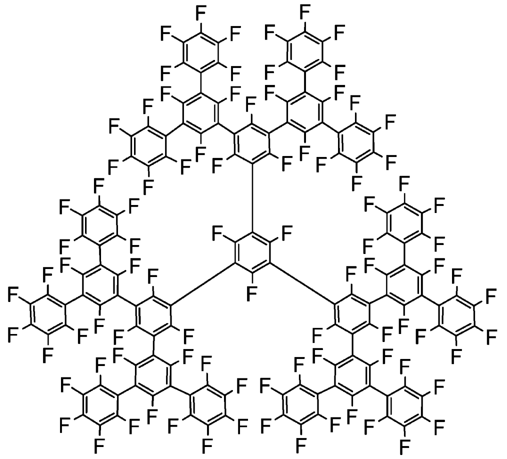
n = 4



46 **a n = 4**
b n = 3
c n = 2



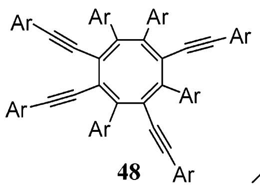
47a



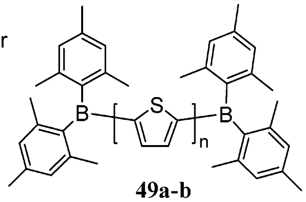
47b

Perfluorinated Materials. Perfluorinated oligo(*p*-phenylene)s, linear (**44a**−**d**, **45**)[80a] and branched (**46a**−**c**),[80b−d] and phenylene dendrimers **47a** and **b**[80b] were developed as ETMs for OLEDs. The linear oligomers (**44a**−**d**, **45**) were insoluble in organic solvents and were highly crystalline solids with no glass transitions.[80a] Compared to Alq_3, the 2 orders of magnitude higher electron mobilities (2×10^{-3} cm²/Vs at 9.4×10^5 V/cm)[80a] in vapor-deposited films of **44b** suggested good prospects for electron transport. The series **44a**−**d** were successfully used as ETMs for Alq_3-based OLEDs giving a brightness of 12 150 cd/m² in the case of **44b**.[80a] The perfluoro-2-naphthyl oligomer **45** was superior to Alq_3 as an ETM, giving a brightness of 19 970 cd/m² at low voltages (10 V).[80a] The branched oligomers **46a**−**c** were soluble in organic solvents and were amorphous with T_gs of 135−176 °C.[80b,c] With increase in π-conjugation from **46c** to **46b** to **46a**, the T_gs and EAs also increased and consequently **46b** was a better ETM than **46c**. Nondispersive electron transport was noted in **46c** with a mobility of 2.3×10^{-4} cm²/V s (at 6.3×10^5 V/cm).[80c] Molecule **46c** had a large optical band gap (4.0 eV), high IP (6.6 eV), and low EA (2.6 eV), resulting in hole/exciton blocking properties superior to those of BCP (**38b**) and giving rise to highly efficient phosphorescent OLEDs.[80d] The branched structure of dendrimers was expected to give amorphous solids; however, soluble dendrimers **47a** and **b** were highly crystalline (T_m = 277 °C and 426 °C, respectively).[80b] As ETMs for Alq_3 OLEDs, they gave inferior performance compared to the linear (**45**) or branched (**46a**) oligomers with very low brightnesses of ~30 cd/m² at high voltages (>20 V). Cyclic voltammetry studies revealed irreversible reductions for **47a** and **b** and rather low EAs (~2.2 eV).[80b] Due to the very low degree of conjugation in the perfluorinated dendrimers (steric hindrance of bulky fluorine atoms) and low EAs, they appear to be inferior ETMs compared to the linear/branched structures.

Other Promising ETMs. New ETMs for OLEDs are constantly being developed. Octasubstituted cyclooctatetraenes (**48**, COTs) were specifically made as ETMs for blue OLEDs.[81] They had reversible reductions with EAs >2.45 eV and large optical band gaps (>3.2 eV), indicating high IPs and good hole-blocking properties. Amorphous, thermally stable films could be vapor deposited owing to their high T_g ~214 °C.[81] Using **48** as the ETM for blue-emitting OLEDs based on *N,N′*-diphenyl-*N,N′*-dinaphthylbenzidine, moderate EQEs of 0.1−0.2% and a brightness of 280 cd/m^2 at 18 V were achieved.[81]



48
Ar = *p*-tolyl



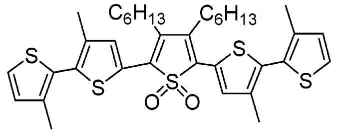
a n = 2
b n = 3

49a-b

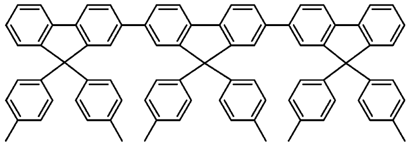
New ETMs based on dimesitylboryl moieties such as **49a** and **b** were recently reported.[82] These molecules formed amorphous films by vacuum evaporation (T_g = 107 and 115 °C, respectively) and showed reversible two-peak reductions with high EAs (~3.05 eV).[82a] Using **49b** as the ETM for Alq$_3$ OLEDs, a brightness of 21 400 cd/m^2 and an EQE of 1.1% were obtained, compared to 13 000 cd/m^2 and 0.9% for OLEDs without **49b**.[82a] Efficient blue-green EL has also been reported from fluorescent bipolar molecules based on dimesitylboryl and triphenylamine groups.[82b]

Several oligothiophene-*S*,*S*-dioxides (**50**) have been reported using the approach of selective dearomatization of the thienylene rings in oligothiophenes.[83] Electrochemical studies of all derivatives containing *S*,*S*-dioxides showed higher EAs (>3.0 eV) than unsubstituted oligothiophenes.[83a,b] Improvements by factors of ~5−20 in solid-state fluorescence quantum yields were seen by oxidizing the sulfur atom on the central thienylene ring in a thiophene pentamer (37% for **50** vs 2% for quinquethiophene).[83a] Blend OLEDs using **50** as an emissive ETM showed red EL (620 nm) with moderate brightness of ~200 cd/m^2 at low voltages (7 V).[83a] Recent reports have showed that very high brightness (~10 500 cd/m^2) OLEDs can be made with spin-coated thin films of branched thiophene oligomers as the emissive materials.[83c] Dibenzothiophene-5,5-dioxide has been used in copolymer architectures as a possible emissive material with enhanced electron transport properties, although none have thus far been used as an ETM.[84]

The prospect that molecular building blocks other than electron-deficient heterocyclic rings, or the use of electron-withdrawing groups, can be used to achieve electron-transport capability in organic materials was demonstrated by the high electron mobility (~1.2 × 10^{-3} cm^2/Vs at 6.5 × 10^5 V/cm) seen in amorphous thin films of the hydrocarbon ter(9,9-diarylfluorene)s (**51**).[85a] This molecule showed reversible reductions with EA of ~2.4 eV and high brightness blue EL (>5000 cd/m^2) was demonstrated.[85b]



50



51

Toward Efficient Single-Layer OLEDs. Instead of bilayer or multilayer diodes with a separate ETM layer, an alternative strategy to achieving balanced charge injection and transport in OLEDs is through blending of an ETM with an emissive material.[58b,86a] Although this approach has successfully been explored, as exemplified by binary blends of **28e** with MEH−PPV or poly(3-octylthiophene),[58b] the control of phase separation and morphology in such blends remains a challenge.[58b,86]

Ideally, the functions of hole-transport, light emission, and electron-transport would be designed into one material, thereby facilitating balanced charge injection and transport in single-layer OLEDs. Toward this end, electron-transport (n-type) moieties have been incorporated into emissive p-type organic materials and thereby creating essentially bipolar emissive materials. Bipolar small molecules based on n-type moieties such as oxadiazoles, dimesitylboryls, or benzothiadiazoles in combination with p-type triarylamines or fluorenes have been reported.[87] However, multilayered OLED structures with separate HTLs/ETLs were still needed to achieve good device performance (high brightness and high efficiency) from current bipolar small molecules. Besides, the emission characteristics of the parent emissive component can be significantly altered by exciplex formation in some bipolar molecules.[87a] The strategy of creating bipolar (or donor/acceptor) materials is more readily implemented by polymerization or copolymerization since the n-type moieties can be incorporated either directly into a p-type polymer backbone[49b−d,58d−e,88,89d−e,92] or as pendants to the main chain.[89a−c,90,91,93] Emissive copolymers of hole-transporting backbones such as fluorene, carbazole, and phenylene vinylene, with n-type moieties such as oxadiazole,[88a−b,89−91,93] quinoline,[58a−e,88b−c] quinoxaline,[88b] cyano groups,[76−79,92] and benzothiadiazole[49b−d] have been reported. To attain the perfect balance between hole and electron injection and the desired EL color, the choice of the particular p-type/n-type pair, the point of attachment of the n-type moiety to the p-type backbone, and the relative ratios of the two moieties need careful consideration.

A widely investigated p-type/n-type pair is poly(phenylenevinylene)/oxadiazoles. Polymers **52a** and **b** with pendant oxadiazole units linked to the phenylene ring were soluble in organic solvents and showed a 16- and 56-fold enhancement in EQE compared to PPV in single-layer LEDs, respectively.[90a] The enhanced electron injection/transport properties due to the pendant oxadiazole units resulted in high brightness (1090 and 7570 cd/m^2) from single-layer OLEDs from **52b** with Al:Li and Ca cathodes, respectively.

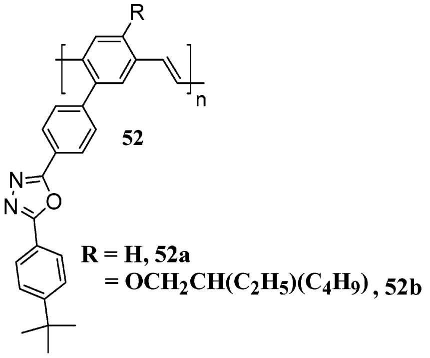
Table 1. Properties of ETMs for OLEDs: Electron Affinity/Ionization Potential Levels (EA/IP), Glass Transition Temperature (T_g), and Device Performance (Brightness and Efficiency) Based on a Particular Emissive Material

material	EA (eV)^a	IP (eV)^a	T_g (°C)	emissive material	brightness (cd/m^2)^b	efficiency^b	ref
3^c	2.16	6.06	n.o.	PPV	500	0.8%	13a,15a,15c
5a^d	2.8	6.5	n.r.	PPV-based	200	6 lm/W	17b
6a^d	2.69	5.93	n.r.	EM2	19 000	4%	19a
6b^f	3.20	6.50	142	PPV	300	0.1%	19b,20a
6c	n.r.	n.r.	222	PPV	n.r.	0.4%	20a,b
7c^c	2.26	n.r.	125	Alq$_3$	1300	0.7%	21a
10c	2.8	6.2	n.r.	DMOS−PPV	n.r.	0.1%	24c,d
11	n.r.	n.r.	196	MEH−PPV	800	0.26%	25a
12	2.75	5.91	125				25b
13c	n.r.	n.r.	153	PPV	n.r.	~0.04%	27a
14c	n.r.	n.r.	209	PPV	300	0.1%	26b
15b	n.r.	n.r.	220	PPV	n.r.	0.1%	27b
16a	3.0−3.1	5.8−5.95	172	TPD:rubrene	11 750	2.8 cd/A	29c,30,32,35a
16b^d	2.9	5.4	n.r.	TPD:rubrene	16 602	3.5 cd/A	35a
16c^d	3.4	5.7	n.r.	TPD:rubrene	19 539	4.3 cd/A	35a
17b	~3.1	~5.4	n.r.	rubrene	35	n.r.	36c
18^d	2.65	5.41	n.o.	Alq$_3$	n.r.	1.96 cd/A	37
19a^c	~2.3	n.r.	n.r.	Alq$_3$	5800	n.r.	38a−b
20^{c,j}	2.48	n.r.	115	Alq$_3$	~1000	n.r.	42a
21d^c	2.86	6.16	232	PPV	50	n.r.	42b
22^d	2.7	6.2−6.7	n.r.	Ir−Phosphor	~10 000	10.4%	44a−b,45a
23a	2.7	5.5	> 400	MEH−PPV	1400	2.5%	46c,48b
23b	3.0	5.3	> 400	MEH−PPV	429	0.55%	46c,48b
23c	2.8	5.2	> 400	MEH−PPV	587	0.65%	46c,48b
24	2.4	5.7	> 400	MEH−PPV	970	1.9%	46c,48b
25^e	3.2−3.5	5.9	n.r.	**25**	~10 000	14.5 cd/A	50a,b
26	2.9−3.5	5.7−6.3	n.r.	PPV	~900	0.25%	51a−c,52a−b
27^d	4.3	6.7	n.r.	**27**	n.r.	0.08%	51d
28a	2.50	5.47	> 300	PPV	138	~0.1%	10a, 12a
28b	2.42	5.49	> 300	PPV	826	~0.6%	10a, 12a
28d^e	3.21	6.0	214	MEH−PPV	167^g	0.035%	58d−e
28e	3.0	5.50	247	MEH−PPV	~2300	0.68%	58a
30b	2.57	5.27	> 300	MEH−PPV	700	0.56%	59a−b
31^c	~2.76	5.86	106	PPV	205	0.01%	61a
32^c	~2.76	5.96	147	PPV	192	0.10%	20b,61a
33^c	2.56	6.26	155	EHO−OPPE	~260	0.14 cd/A	62
34b^d	3.24	5.94	> 250	PPV	~45	~0.04%	63a
35a^{e,k}	3.3	6.7	n.r.	PPV	~250	0.35%	63b
35b	3.0	5.54	> 300	PPV	710	0.4%	63c
36a^j	3.10	5.85	> 300	MEH−PPV	690	1.3%	64
36b^j	3.01	5.65	> 300	MEH−PPV	595	3.1%	64
36c^j	2.90	5.65	> 300	MEH−PPV	579	2.9%	64
36d^j	2.98	5.70	> 300	MEH−PPV	965	1.1%	64
37a	2.83	5.27	> 300	PPV	46	0.02%	10a, 12a
37b	2.86	5.34	> 300	PPV	46	0.02%	10a, 12a
37c	2.87	5.06	> 300	PPV	19	0.01%	10a, 12a
38a^d	3.2	6.5	62				67,68b
39c	n.r.	n.r.	81	Alq$_3$	~20 000	2.7 cd/A	73a
39d^d	3.3	n.r.	n.r.	Alq$_3$	~1000	2.6 lm/W	71b
40a^d	~3.1	6.1	n.r.	Alq$_3$	~10 000	n.r.	74a
41b	n.r.	n.r.	n.r.	Alq$_3$	~16 000	n.r.	74c
42a	3.02	5.55	n.r.	**42a**	2.6^h	4%^{i}	24d,76a
43	n.r.	n.r.	~45	**43**	3000	n.r.	79
44b	n.r.	n.r.	n.o.	Alq$_3$	12 150	n.r.	80a
45	n.r.	n.r.	n.o.	Alq$_3$	19 970	n.r.	80a
46a^c	2.62	n.r.	176	Alq$_3$	~1500	n.r.	80c
46b^c	2.60	n.r.	161	Alq$_3$	4380	n.r.	80c
46c	2.56	6.56	135	Alq$_3$	2860	n.r.	80b−d
47a	~2.20	n.r.	125	Alq$_3$	~30	n.r.	80b
47b	~2.20	n.r.	n.r.	Alq$_3$	~30	n.r.	80b
48^c	~2.47	5.72	214	Perylene:NPD	280	~0.16%	81
49a	~3.0	n.r.	107	Alq$_3$	21 400	1.1%	82a
49b	~3.0	n.r.	115	Alq$_3$	23 200	1.1%	82a
50	~3.10	~5.3−5.4	n.r.	**50**	~200	1.3%	83a,b
51	~2.4	~5.7	n.o.	**51**	~5400	2.5−3%	85b
52a^d	3.93	6.42	> 300	**52a**	n.r.	0.003%	90a
52b^d	3.98	6.32	> 300	**52b**	1090	0.045%	90a
53	2.87	5.06	n.r.	**53**	5140	0.43%	90b
54	2.83	5.0	n.r.	**54**	15 000	2.27 cd/A	91a
55^e	3.21	5.57	171	**55**	19 395	21.1 cd/A	91b
56	3.16	4.96	159	**56**	2100	0.05%	92b
57	2.88	5.26	n.o.	**57**	600	0.85 lm/W	92c

Table 1 (Continued)

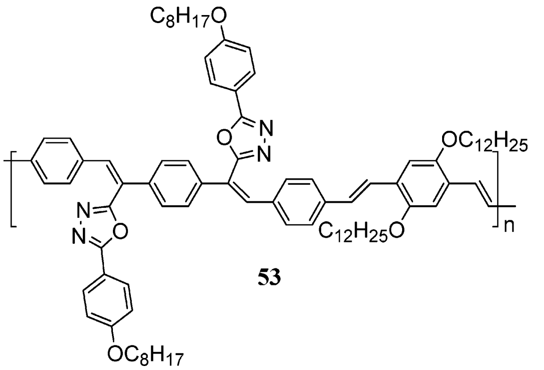
material	EA (eV)[a]	IP (eV)[a]	T_g (°C)	emissive material	brightness (cd/m^2)[b]	efficiency[b]	ref
58	3.27	5.42	80	**58**	21 000	1.5%	49d
59	2.23	5.52	213	**59**	2770	0.52%	93a
60	2.30	5.06	166	**60**	4080	1.21%	93b

[a] Wherever possible, EA/IP values were recalculated from reported literature values as EA/IP = $[E_{\text{onset}}]^{\text{red/ox}}$ (vs SCE) + 4.4, by converting onset potentials to versus SCE [E (SCE) = E (Fc$^+$/Fc) + 0.1588]. [b] Maximum brightness and efficiency. Unless otherwise indicated, efficiency values are EQEs. For other parameters that affect OLED performance (HTLs, cathodes, anodes) see specific details in reference. [c] EA estimated from formal reduction potential as EA = $[E^{0'}]^{\text{red}}$ (vs Fc$^+$/Fc) + 4.5588. [d] No CV data shown; EA calculated as EA = IP (from UPS) − E_g^{opt}. [e] No reduction data shown; EA calculated as EA = IP (from CV) − E_g^{opt}. [f] IP = EA (from CV) + E_g^{opt}. [g] Brightness in μW/cm^2. [h] Brightness in W sr^{-1} m^{-2}. [i] Internal quantum efficiency. [j] CV experiment done on sample thin film. [k] CV experiment performed in solution. [l] PPV = poly(*p*-phenylene vinylene), EM2 = triphenylamine-oxadiazole small molecule, DMOS−PPV = poly(2-dimethyloctylsilyl-1,4-phenylene vinylene), MEH−PPV = poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene vinylene), TPD = *N,N'*-diphenyl-*N,N'*-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, EHO−OPPE = 2,5-dialkoxy substituted poly(*p*-phenylene ethynylene), NPD = *N,N'*-diphenyl-*N,N'*-dinaphthylbenzidine [m] n.o. = not observed; n.r. = not reported.



52

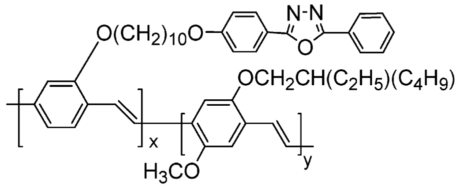
R = H, 52a
= OCH$_2$CH(C$_2$H$_5$)(C$_4$H$_9$), 52b



53

Attachment of the oxadiazole unit to the vinylene linkage of PPV as in **53** gave improved OLED performance.[90b] Polymer **53** had EA and IP of 2.87 and 5.06 eV, respectively. These values are comparable to those of MEH−PPV, suggesting that the pendant oxadiazole units do not significantly affect the LUMO level of the copolymer. Single-layer ITO/PEDOT/**53**/Al diodes showed a bright yellow emission with 0.34% EQE and a brightness of 1457 cd/m^2. Replacing Al with Ca cathode gave a better performance (0.43% EQE and 5140 cd/m^2 brightness).[90b] However, incorporation of oxadiazole moieties directly into the PPV backbone can significantly lower the LUMO level of the copolymer, transforming the copolymer into an n-type material as indicated by the irreversible oxidations and reversible reductions in their cyclic voltammograms.[89e]

A series of copolymers **54** was synthesized where the oxadiazole unit was separated from the polymer backbone by a long alkoxy chain.[91a] At the optimum copolymer composition ($x = 0.37$, $y = 0.63$), single-layer LEDs showed a brightness of 15 000 cd/m^2 and an efficiency of 2.27 cd/A, 30 times brighter than single-layer MEH−PPV OLEDs. Cyclic voltammograms of **54** revealed an EA of 2.83 eV, which is comparable to that of MEH−PPV. Recently reported PPV with pendant oxadiazole, **55**, has a high T_g (171 °C) and a high EA (3.21 eV), and was soluble in organic solvents.[91b] Single-layer LEDs of the type ITO/PEDOT/**55**/Al showed a brightness of 19 395 cd/m^2 and efficiency of 21.1 cd/A, which is nearly a 100-fold increase in efficiency compared to PPV without pendant oxadiazole. This yellowish-orange emitting copolymer has one of the highest EL efficiencies among all PPV derivatives investigated to date.



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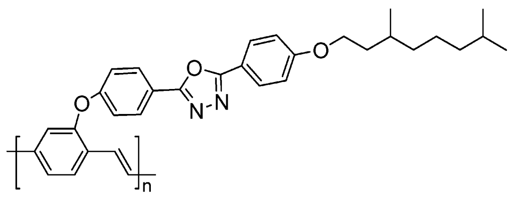

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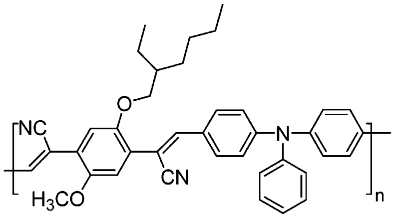

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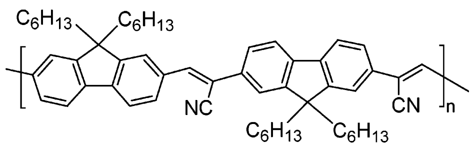
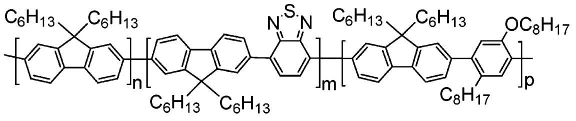
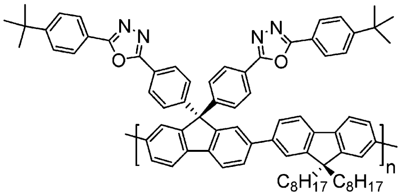


57

Cyano substituents have also been effectively used to impart n-type characteristics to PPV, with poly(cyanoterephthalydine)s (**42a** and **b**, and **43**)[76−79] being earlier examples. The incorporation of cyano groups at the vinylene linkages in PPV is thought to enhance the EA and the anion stability. Polymer **56** showed both reversible oxidation and reduction, suggesting the potential for bipolar charge transport properties.[92b] It had an IP of 4.96 eV and an EA of 3.16 eV. Single-layer ITO/**56**/Al OLEDs showed bright orange-red EL (2100 cd/m^2, 0.05% EQE). CN−Poly(dihexylfluorenevinylene) **57** had an EA 0.27 eV higher compared to that without cyano substituents.[92c] Green EL with a brightness of 600 cd/m^2 was achieved from ITO/PEDOT/**57**/Al diodes, a 2-fold improvement over the polymer without cyano groups.



58 [n = 0.5, m = 0.25, p = 0.25]



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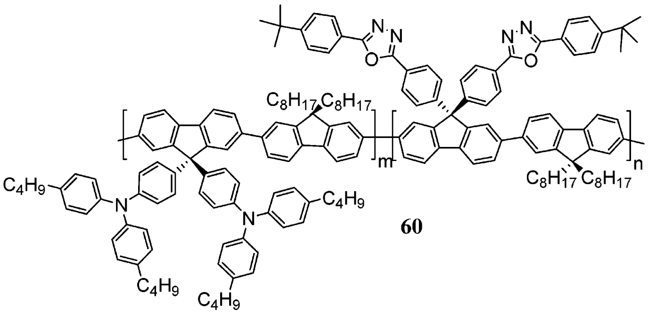

60

Fluorescent green copolymers of fluorene with n-type moieties such as benzothiadiazole (**25** and **58**)[49d,50] have been reported. Copolymer **58** showed an EA of 3.27 eV, which is ~0.7−1.0 eV higher compared to the polyfluorene homopolymer. Efficient green EL (533 nm) was achieved from single-layer OLEDs based on **58**, using a PEDOT hole injection layer and a calcium cathode, with a maximum brightness of 21 000 cd/m^2 and EQE of 1.5%.[49d] In such fluorene copolymers, although efficient EL with high brightness is achieved, the blue emission of the parent polyfluorene backbone is lost due to efficient energy transfer from the high band gap fluorene units to the low energy n-type moieties such as benzothiadiazole.

Attaining pure blue EL with enhanced brightness and efficiency from the polyfluorenes remains a challenge.[4c−e] Polyfluorenes with pendant oxadiazole units (**59** and **60**) have been investigated for enhanced electron injection.[93] Attaching two 1,3,4-oxadiazole units at the sp^3-hybridized C-9 atom of fluorene prevents strong electronic interaction between the pendant oxadiazole and the polyfluorene backbone, thus retaining the native blue emission. The electronic structure of polyfluorene is not affected by the side-chain oxadiazoles as indicated by the similar EAs (~2.23 eV) of **59** and PFO. Bright blue EL (2770 cd/m^2) with 0.52% EQE was obtained from single-layer OLEDs, ITO/PEDOT/**59**/Ca/Ag.[93a] To further improve hole injection, copolymer **60** with both pendant triphenylamine units and oxadiazole units has been studied.[93b] Copolymer **60** retained blue emission and had an IP (5.06 eV) that was lower by 0.46 eV compared to that of **59**, suggesting improved hole injection due to the triphenylamine substituents. Both **59** and **60** showed improved thermal stability with T_gs of 213 and 166 °C, respectively, significantly better than that of PFO (~51 °C). A brightness of 4080 cd/m^2 and an EQE of 1.21% were achieved from ITO/PEDOT/**60**/Ca/Ag.[93b]

Table 2. Electron Mobility in Selected Electron Transport Materials

compound	mobility, μ_e (cm^2/Vs)[a]	electric field, E (V/cm)	ref
3 (PBD)[b]	1.9×10^{-5}	1×10^6	**16b**
4 (BND)[c]	2.2×10^{-5}	7.5×10^5	**16a**
5a[b]	2.1×10^{-5}	1×10^6	**16b**
6b[c]	1.2×10^{-6}	7×10^5	**19b**
16a (Alq$_3$)[d]	$\sim 1 \times 10^{-5}$	$0.39{-}1.3 \times 10^6$	**33a**
23a[e]	$\sim 2 \times 10^{-7}$		**48a**
25	$\sim 1 \times 10^{-3}$	5×10^5	**50a**
32	$\sim 1 \times 10^{-4}$	$\sim 1 \times 10^6$	**61b**
38a	5.2×10^{-4}	5.5×10^5	**66**
38b[b]	1.1×10^{-3}	1×10^6	**16b**
39d	$\sim 2 \times 10^{-4}$	6.4×10^5	**71a**
44b	2×10^{-3}	9.4×10^5	**80a**
46c	2.3×10^{-4}	6.3×10^5	**80c**
51	$\sim 1.2 \times 10^{-3}$	$\sim 6.5 \times 10^5$	**85a**

[a] Mobilities are from the time-of-flight method unless otherwise stated. [b] Mobility estimated from SCLC measurements. [c] 50 wt % in polycarbonate. [d] 150-nm thin Alq$_3$ films. [e] Mobility estimated from FET measurements.

These copolymers highlight the potential of combining charge transport and emissive functionalities into one material for OLED applications. Achieving balanced hole and electron injection/transport in one material greatly simplifies device fabrication. However, judicious choice of the hole- and electron-transporting moieties is needed to obtain targeted emission colors from the copolymers, making design and synthesis of such multifunctional copolymers a challenging task for the materials chemist.

3. Conclusions and Outlook

Much progress has been made in the synthesis, development, and application of electron transport materials as a means to improve OLED performance through enhanced electron injection and transport. Many different classes of ETMs have been investigated. Some of the key properties of representative ETMs discussed here are summarized in Tables 1 and 2. The effectiveness of an organic material, either low molar mass or polymeric, as an electron transport material for OLEDs is determined by a delicate interplay between various properties of the ETM such as the EA/IP, electron mobility, thermal stability, and electrochemical stability. It is difficult to identify the best class of ETMs based on OLED performance alone given that it is influenced by many factors such as device geometry, choice of cathode/anode, the p-type emissive material, and OLED testing conditions; however, some general observations can be made. Most current ETMs have EAs ≤3.2 eV since this provides the best match with the LUMO levels of the most common p-type emissive materials (e.g., PPV and MEH−PPV) for the green and red-orange spectral range. To act as an ETM for blue

OLEDs, a large band gap ≥3.2 eV material, such as **22** and **48**, is needed to avoid energy transfer to and light emission from the ETM. The perfluorinated molecules (**44**−**47**) with very large band gaps ≥4 eV and EAs ≤2.6 eV could be possible ETMs for blue OLEDs. However, the use of an ETM with a large band gap and moderate electron affinity may not be the most effective for electron injection from air-stable cathodes such as Al (Φ_c = 4.3 eV). One possible strategy is to use two different ETMs with the higher EA (>3 eV) one in contact with the cathode.

Regardless of the spectral region of interest, all next-generation ETMs for OLEDs should have T_gs as high as possible, preferably greater than 150 °C, to improve the stability and durability of the devices. The thermally robust polyquinolines (**28a**−**e** and **30a**−**f**), polybenzobisazoles (**23a**−**c** and **24**), and diphenylanthrazolines (**36a**−**d**) with T_g > 200 °C give very stable repeatable performance as ETMs in OLEDs, whereas OLEDs using siloles (**39b**, **40a** and **b**; T_g < 90 °C) as the ETMs degrade at higher electric fields due to melting/crystallization of the ETM layer. Increasing the bulk of the molecule using branched (**6b**, **7c**, **32**, **46a**−**c**), spiro (**33** and **51**), or dendrimer (**6c** and **47a**) architectures is an effective strategy to enhance the thermal stability (T_g) of the ETM as well as its processability (solvent solubility).

Although the molecular design criteria for achieving a desired EA value and a high T_g in an ETM are well understood, the control of electron mobility (μ_e) is yet to be attained. In fact, detailed characterization of the electron mobility of most current ETMs is lacking, as is understanding of the underlying structure−μ_e relationships that could guide the design of next-generation ETMs for high-performance OLEDs. The μ_e values of all current ETMs are rather low, being in the range of 10^{-7} to 10^{-3} cm^2/Vs (Table 2). Higher electron mobilities are desirable in ETMs, particularly for OLEDs targeted for high brightness display and lighting applications. Some of the design factors essential to achieving high electron mobilities in organic semiconductors are large electron affinities with facile reversible electrochemical reductions, stiff crystalline molecules with strong intermolecular interactions, and ordered solid-state morphology. Fused heterocyclic molecules such as perylene diimides[94a] or benzobisimidazole benzophenanthroline represent ideal building blocks toward this end. For example, the highest electron mobility (0.1 cm^2/Vs) *in air* yet reported in an n-type conjugated polymer was achieved in spin-coated films of the ladder polymer poly(benzobisimidazobenzophenanthroline) (BBL) with an EA of 4 eV and efficient π-stacking.[11f] Perfluorination is also an effective tool in achieving enhanced EA as demonstrated by the high electron mobilities obtained in fluorinated CuPc[94b] and oligothiophenes.[94c]

Successful commercial applications of OLED technology in the next several years will mean increasing attention to a related but much tougher challenge of realizing organic diode lasers (ODLs).[95] Some of the possible ODL architectures that have been analyzed theoretically, as in OLED configurations, require ETMs that will support very high current densities (∼10^6 mA/cm^2) and thus must have very high electron mobilities ($\mu_e \gg 10^{-3}$ cm^2/Vs).[95] Clearly, one of the important future research directions in the field should be the achievement of ETMs that combine high electron mobility, high T_g, and a suitable electronic structure (electron affinity and optical band gap).

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