

# Solution processable small molecules for organic light-emitting diodes

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Organic light-emitting diodes (OLEDs) based on vacuum deposited small molecules have undergone significant progress since the first efficient double-layered OLEDs were reported in 1987 by Tang and Van Slyke. Recently, solution processed small molecular OLEDs are also drawing more and more research attention, as such a technology combines advantages of the facile synthesis of small molecules and the low-cost solution process like polymers. The performance of OLEDs made by solution process is gradually catching up with their vacuum deposited counterparts. This feature article will review the device structures adopted to achieve high performance solution processed OLEDs, the development of solution processable small molecules, and the comparisons of the different nature of the films and devices fabricated by solution-process or by vacuum deposition. Finally, the prospects and remaining problems will be discussed.

## 1. Introduction

Organic light-emitting diodes (OLEDs) have drawn intense attention during the past decades due to their potential applications in solid-state lighting and flat-panel displays.<sup>1–6</sup> Generally, there are two approaches to fabricate devices: for OLEDs based on small molecules, the standard fabrication method is vapor deposition under vacuum;<sup>1</sup> for polymeric materials, simple solution process such as spin-coating or ink-jet

printing can be utilized.<sup>2</sup> Small molecules have advantages such as easy synthesis and purification, and the vapor deposition techniques allow the fabrication of complicated multiple layers with excellent device performance.<sup>7–11</sup> However, thermal evaporation process under high vacuum increases fabrication complexity and makes the utilization of the expensive OLED materials very low (~20%).<sup>12</sup> Additionally, pixelation using evaporation masks would limit its scalability and resolution.<sup>13</sup> The best way to improve the efficiency of the process and reduce the production cost is to use solution process for the fabrication of OLEDs. For example, ink-jet printing can be effectively used to fabricate large-area, high-resolution full-color flat-panel displays.<sup>14,15</sup> On the other hand, although light-emitting polymers are considered to be suitable for solution process, their performances are lower than vacuum deposited small molecules.

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The efficiency and lifetime of polymer-based devices need to be further improved for applications in commercial active-matrix OLED devices, whilst there are some intrinsic difficulties such as the control of batch-to-batch variations and the purification of the polymeric materials. Therefore, it is a good strategy to develop OLEDs based on solution processible small molecules, which would open up exciting possibilities for commercialization of printed OLEDs for displays and lighting. However, unfortunately, a large majority of the small molecules designed for vacuum deposition are not suitable for the solution process due to poor film morphology and easy crystallization upon spin-casting. At this stage, development of small molecules for solution processible OLEDs and optimization of the devices structure as well as the device fabrication process are of high importance for solution processed OLEDs in order to catch up with their evaporated counterparts.

In this feature article, we will first review the device structures adopted to achieve high performance solution processed OLEDs. Then, we will summarize the development of solution processible small molecules. Comparison of the difference between the solution-processed small molecule films (devices) and the vacuum deposited small molecule films (devices) will be also discussed.

## 2. Device structure

### 2.1 Single-layer devices

The simplest structure of solution-processed small molecule OLEDs contains only one emitting layer, sandwiched between the anode of indium tin oxide (ITO) and the cathode. Although the ITO anode has high optical transparency, it has still some drawbacks such as poor film morphology and low surface work function. For polymeric OLEDs, the “standard” device structure has a hole injection layer of chemically doped conjugated polymers, such as polypyrrole,<sup>16</sup> polythiophene derivatives<sup>17,18</sup> or polyaniline.<sup>19,20</sup> These doped polymers not only flatten the rough ITO surface but also lower the barriers for hole injection to the emitting layer due to their high work functions, leading to improved device efficiency, device uniformity, and prolonged device lifetime. For solution processed OLEDs based on small molecules, the water dispersion of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) is the most widely used anode buffer layer. However, PEDOT:PSS is not an ideal material for the hole injection layer due to the following issues: first, PEDOT:PSS has a work function of 5.0–5.2 eV, which is still not high enough for hole injection into the layers of most of emitting polymers and emitting small molecules; second, it is strongly acidic (typical pH value of 1.58) so that it can etch the ITO anode and then In and Sn can migrate into the active layer of the device during operation. Recently, Lee *et al.* reported that a new conducting polymer composition composed of PEDOT/PSS and a perfluorinated ionomer (PFI) can have a very high work function up to 5.95 eV which is significantly higher than that of PEDOT:PSS.<sup>21</sup> The use of PEDOT:PSS/PFI as a hole injection layer in PLEDs greatly improved the device efficiency (*ca.* 2 times) and the lifetime (*ca.* 50 times). So *et al.* also reported that polythienothiophene (PTT) doped with a perfluorinated

ionomer, poly(perfluoroethyleneperfluoroethersulfonic acid) (PFESA) can have a work function ranging from 5.2 eV to 5.7 eV and the device using the composition as the hole injection buffer layer in small molecule OLEDs showed improved device efficiency and lifetime.<sup>22</sup> All these features make the high work function buffer layers (PEDOT:PSS/PFI and PTT:PFESA) promising candidates for solution processed OLEDs based on small molecules.

For single-layer devices, it is necessary to include the function of transporting both the holes and electrons into a single emitting layer (EML). This may be achieved by mixing the hole- and electron-transporting molecules. Samuel and coworkers reported a highly efficient single-layer OLED based on small molecules.<sup>23</sup> An iridium complex was blended with the mixed-host of 4,4'-bis(N-carbazolyl) biphenyl (CBP) and 1,3,5-tris(2-N-phenylbenzimidazolyl) benzene (TPBI) in CHCl<sub>3</sub> solution. The single-layer devices were formed by spin coating the CHCl<sub>3</sub> solution onto O<sub>2</sub> plasma treated ITO substrate. A maximum power efficiency of 12.8 lm/W was measured at 8.1 V and 550 cd m<sup>-2</sup>. The authors suggested that, by simple blending of hole and electron-transporting molecules, highly efficient light-emitting diodes can be made with a very simple device structure.<sup>23</sup>

Still, problems such as physical separation may occur in these blend systems. In this regard, it is an exciting way to design and synthesize small molecules with balanced ambipolar transporting properties. For example, Bryce and coworkers reported chemically tailored functional molecules for balanced charge-injection and charge-transport.<sup>24</sup> They designed bipolar 2,5-diaryl-1,3,4-oxadiazole-fluorene hybrids which incorporate triphenylamine or carbazole units within the  $\pi$ -electron system. With such materials, single-layer devices with good performance have been fabricated *via* solution process.

### 2.2 Multilayer devices

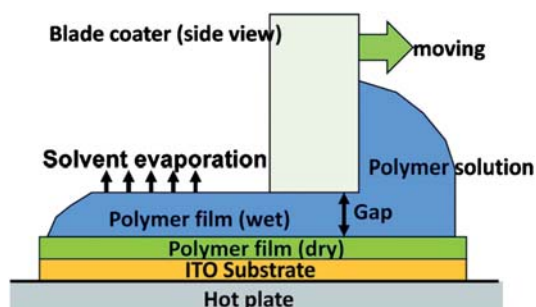
To ensure high performance, it is important to balance the injection of holes and electrons in OLEDs and to confine the excitons in the emissive layer. This is conventionally achieved by stacking different layers such as transport layers, carrier blocking layers, and emissive layers in a tight configuration. However, it is difficult to form multilayer structures by the solution process because of the dissolution of the former layer by the later solution. A compromised way is to make the EML by solution process and then to vacuum evaporate the exciton blocking layer (EBL) and the electron transporting layer (ETL). This approach is extremely useful for phosphorescent OLEDs, as triplet excitons have longer lifetime. It is important to confine triplet excitons in the EML by EBL to ensure high efficiency.

One straight forward way to fabricate multilayer structure OLED by solution process is to find suitable solutions for each function layer so that the later solution will not dissolve the former layer. Elschner *et al.* fabricated three-layer OLEDs by subsequently spin-coating two layers onto PEDOT:PSS.<sup>25</sup> The hole-transport-layer (HTL) of methoxy-substituted 1,3,5-tris[4-(diphenylamino)phenyl]-benzene (TDAPB) was spin-coated from tetrahydrofuran solution. The Ga complex emitting layer was formed on top of the PEDOT-PSS/TDAPB layer by spin coating its CH<sub>3</sub>OH solution. Comparable performances were

obtained for the solution processed and vacuum evaporated devices.

Another approach reported by Meerholz *et al.* is to convert a soluble precursor into an insoluble polymer film by cross-linking.<sup>26</sup> Triarylamine-based hole transporting monomers with oxetanes as reactive units can be cross-linked by cationic ring-opening polymerization. On top of the PEDOT:PSS layer, *N,N'*-bis (4-(6-((3-ethyloxetan-3-yl) methoxy)-hexyloxy) phenyl)-*N,N'*-bis (4-methoxyphenyl) biphenyl-4,4'-diamine (QUPD) with a photoacid concentration of 2 wt% was spin-coated and then cured to form a cross-linked HTL (X-HTL). Then, *N,N'*-bis (4-(6-((3-ethyloxetan-3-yl)methoxy))-hexylphenyl)-*N,N'*-diphenyl -4,4'-diamine (OTPD) was prepared with a photoacid concentration of 0.5 wt%. An electron transporting small molecule host doped with an iridium complex was then spin-coated as the EML. They compared two kinds of devices: type I [ITO/PEDOT/EML/CsF/Al] and type II [ITO/PEDOT/QUPD (20 nm)/OTPD (10 nm)/EML/CsF/Al]. Type II devices (with double X-HTL) are about three times more efficient compared to type I devices (without X-HTL). And at voltages below 3 V, the leakage current is reduced by about one magnitude in type II devices, indicating of the electron-blocking capabilities of the X-HTL in this type of electron-predominating device. The pronounced increase of the electroluminescence by the introduction of the X-HTLs was attributed to an improved charge-carrier balance and/or to the shift of the recombination zone away from the anode toward the center of the device.

Tseng *et al.* fabricated solution processed multilayer devices by blade coating.<sup>27</sup> The working principle of the multilayer fabrication process by blade coating is shown in Fig. 1. Heating during blade coating was needed to ensure the second film to be dried quickly before the solvent dissolving the first layer. This concept was first developed for polymer OLEDs. Recently, Tseng *et al.* successfully fabricated 4-layered OLED by all-solution-process.<sup>28,29</sup> A 40 nm HTL of *N,N'*-bis(naphthalen-1-yl)-*N,N'*-bis(phenyl)-9,9-dimethyl-fluorene (DMFL-NPB) was blade and spin coated from a chlorobenzene solution upon the PEDOT:PSS layer. The EML of 2 wt% 4,4'-(1E,1'E)-2,2'-(naphthalene-2,6-diyl) bis(ethene-2,1-diyl)bis(*N,N'*-bis(4-hexylphenyl)aniline) (LT-N632) in a host of 1-(7-(9,9'-bianthracen-10-yl)-9,9-dioctyl-9H-fluoren-2-yl)pyrene (LT-N492) was dissolved in chlorobenzene and blade coated to form a 50 nm film on top of DMFL-NPB. The HTL and EML were baked at 120 °C for 10 min and 125 °C



**Fig. 1** Schematic working principle of multilayer structure by blade coating; the process of the second layer is on a hot plate. The solvent of the second layer is quickly evaporated without dissolving the first layer. From ref. 27.

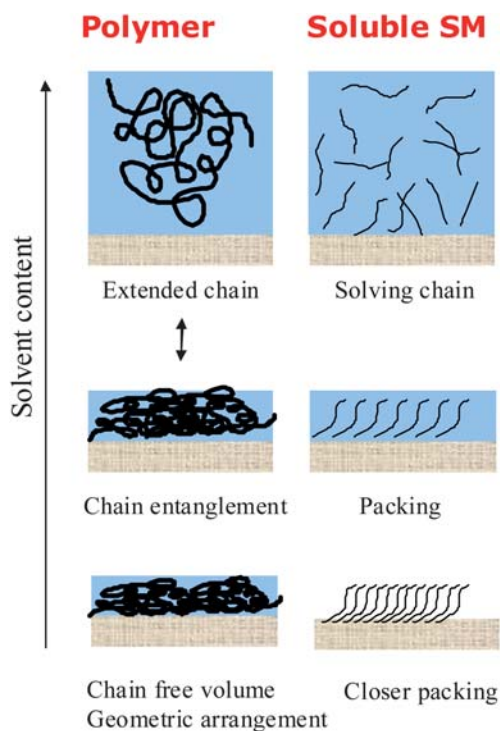
for 5 min in vacuum. The ETL of TPBi was dissolved in methanol to form a 20 nm film by blade and spin coating.

Lee *et al.* developed a soft contact lamination method for fabricating OLEDs by solution-based process.<sup>30</sup> They reported a transfer method of spin-coated small molecule films to fabricate multi-layer OLEDs.<sup>30</sup> The approach involves dissolving a small molecule organic in a solvent, spin coating it on a mold, and then transferring the layer onto the existing organic layer on a substrate. The approaches to form multilayer OLEDs by solution processing allow one to take advantage of both the high efficiency offered by the multilayer structures and the low cost fabrication by solution processing.

### 3. Solution-processed small molecular materials

Polymers have been long known to have the capability to form excellent films from solution. However, polymers and small molecules behave differently during the coating process, as depicted in Fig. 2.<sup>31</sup> The polymer chains are extended in dilute solutions and they would entangle with each other as the solvent gradually dries out. There would still be chain free volume and therefore chain relaxation motion even after the evaporation of the solvent. For small molecules, during the coating process, there is no such entanglement and only the packing density is changed. Therefore, it is important to control the intermolecular interactions by molecular modification to form pin-hole free films of small molecules.

How do you get small molecules with good solubility and film formation ability? The incorporation of alkyl or alkoxy groups is useful for enhancing the solubility. Thin film phases prepared by wet process are presumably possible for most soluble small



**Fig. 2** Schematic picture of the behavior of polymers and small molecules during coating process with the drying of solvent contents.

molecules due to the formation of intermolecular hydrogen bonding or physical entanglement.<sup>32,33</sup> Additionally, the intermolecular hook-like nature of flexible groups randomly dispersed in the solvent matrix, will be beneficial for forming amorphous film phases *via* a wet process.

High thermal stability of the solution-processed films is also required. Generally, small molecules are easy to crystallize due to their low glass transition temperatures ( $T_g$ ). To ensure high  $T_g$ , molecules should possess nonplanar molecular structures, structurally rigid moieties, *e.g.*, biphenyl, naphthalene, fluorene, carbazole, and phenothiazine.<sup>34</sup> The enlargement of molecular size also increases  $T_g$ , thus improving the stability of the films.

Furthermore, good charge transporting or emitting properties are certainly required for charge balance and high-efficiency electroluminescence. The performance of OLEDs generally depends upon the materials functioning in specialized roles such as charge-injecting, charge-transporting, charge-blocking and emitting. In order to obtain high EL quantum efficiency, it is necessary to achieve good charge balance and confine charge carriers within the emitting layer. Recently, solution processable small-molecule OLEDs have achieved great progress in charge-transporting and emitting materials.

### 3.1 Hole-transporting materials

In OLEDs, electrons and holes are injected from opposite electrodes and combine to form spin-singlet or spin-triplet excitons in the emitting layer. The hole-transport layer in layered OLEDs plays the roles of facilitating hole injection from the anode into

the organic layer and transporting holes. Therefore, hole-transport materials should have electron-donating moieties to form stable cation radicals. Fig. 3 shows the chemical structures of some solution processable hole-transporting materials.

Molecules with phenylamine groups have gained much research attention due to their high hole drift mobilities and fortunately most of them are soluble in common organic solvents. However, some of these molecules suffer long-term morphological instability due to their low  $T_g$ . N, N'-di(3-methylphenyl)-N, N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (TPD)<sup>35</sup> and N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB)<sup>36</sup> have been widely used as hole transporters with field dependent hole mobilities of around  $1 \times 10^{-3} \text{ cm}^2/\text{Vs}$ . The  $T_g$ s are 65 °C and 96 °C for TPD and NPB, respectively. TPD and NPB films can be fabricated by spin-coating.<sup>30,37</sup> However, non-uniform surface with high roughness due to crystallization upon thermal treatment of the films is observed.<sup>38,39</sup> Several approaches have been used to overcome this problem. One successful strategy is to blend TPD into polymer matrices like poly(methyl methacrylate) (PMMA), polystyrene (PS), polysulfone, polycarbonate, *etc.* This blending system was found to be able to inhibit crystallization.<sup>40</sup> However, this embedding technique can not always warrant morphological stability because of phase separation. Another approach to prevent crystallization induced degradation is the design of amorphous materials with high glass transition temperatures, enabling the preparation of high quality and morphologically stable films. Besides simple molecular modifications by virtue of bridging, annulation, and substitution at the TPD scaffold, different structural patterns have been examined to provide the required properties. Salbeck *et al.* synthesized spiro-linked structures similar to TPD (spiro-TAD, spiro-MeOTAD) and found significantly enhanced glass transition temperatures indicating increased morphological stability.<sup>41</sup>

Another successful approach to obtain thermally stable amorphous films is to use "starburst" shaped hole transporting molecules, *e.g.*, the families of tris(diphenylamino)-triphenylamine (TDATA), and 1,3,5-tris[4-(diphenylamino)phenyl]benzene (TDAPB). The starburst molecules 4,4',4'''-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA), 4',4'''-tris[2-naphthyl(phenyl)amino]triphenylamine (2-TNATA), have been proven to serve as excellent materials for use in the hole-injection buffer layer.<sup>42,43</sup> m-MTDATA and its analogues are characterised by very low solid-state ionization potentials of 5.0 to 5.1 eV, reversible anodic oxidation to give stable cation radicals, and good quality of their amorphous films prepared by spin coating from solution.<sup>34</sup> Shirota *et al.*<sup>44</sup> found that m-MTDATA/ITO interface is capable of providing trap-free space charge limited current and that m-MTDATA forms nearly an ohmic contact with the ITO electrode.

In comparison, TDAPB has the advantage to resist crystallization due to its steric hindrance by the four central phenyl-groups and the high glass-transition ( $T_g = 112$  °C). Because of TDAPB's high solubility, these molecules can be deposited from solution. Elschner *et al.* reported that TDAPB was used as a buffer-layer between poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) and the emitting layer for ITO/PEDOT:PSS/TDAPB/Alq<sub>3</sub>/Mg : Ag devices.<sup>17</sup> The second layer of spin-coated dendritic phenylamines TDAPB with high glass transition

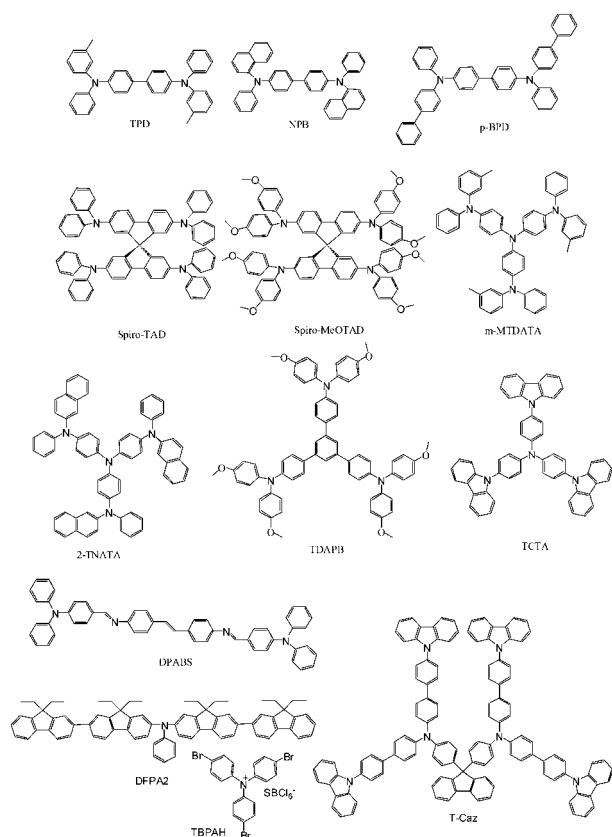


Fig. 3 Molecular structures of hole-transporting materials.

temperature modulates the injection of holes into the emitting layer, formed by evaporated Alq<sub>3</sub>. Compared with 2-layered (without a TDAPB buffer-layer) devices, improvement in efficiency, lifetime and reduction of the electric noise were achieved in the 3-layered device.

Kwon *et al.* found that 4,4',4'''-tris(*N*-carbazolyl)-triphenylamine (TCTA) has good solubility and film forming property.<sup>38</sup> They used it as the interlayer in solution processed OLEDs. Smooth films of TCTA can be obtained by either spin-coating or vacuum deposition. The good amorphous film formation characteristic of the TCTA was ascribed to the three dimensional molecular structure of TCTA. A half sphere shape structure of the TCTA molecule with two coplanar carbazole units and one carbazole unit vertically oriented to the plane containing the other two carbazole units contributes to the amorphous molecular packing, indicating there is no crystallization of the TCTA film during spin-coating and baking process.

Furthermore, Mishra *et al.* described two *tert*-amine-based, non-fluorescent, hole-transport molecules 4,4'-[bis-((4-di-*n*-hexylamino)benzylideneamino)]stilbene (DHABS) and 4,4'-[bis-((4-diphenylamino)benzylideneamino)]stilbene (DPABS) that are suitable for spin-coating on indium tin oxide (ITO) for electronic device, which have HOMO levels comparable to the widely used TPD.<sup>45</sup> However, the electroluminescences of the devices using spin-coated DHABS or DPABS as hole-transporters are weak compared to the standard devices using vacuum evaporated TPD as the hole-transporter. Kido *et al.* used a dichloroethane solution of a soluble and thermally stable arylamine oligomer *N,N*-bis(9,9,9',9'-tetra-ethyl-2,2'-difluorenyl-7-yl)phenylamine (DFPA2) with a Lewis acid (TBPAAH) to form a hole injection layer by spin-coating.<sup>46</sup> The OLED with a emitting layer of tris(8-quinolinolato)aluminium(III) (Alq<sub>3</sub>) showed lower drive voltages and higher power efficiencies, compared with the devices without the hole injection oligomer layer. Ueda *et al.* synthesized a novel thermally stable and hole-transporting amorphous molecule, 9,9-bis(4-[bis(4-carbazol-9-yl-biphenyl-4-yl)-amino]-phenyl) fluorene (T-Caz). T-Caz showed excellent thermal stability ( $T_g = 250$  °C).<sup>47</sup> The device prepared using a spin-coated film of T-Caz onto an ITO coated glass substrate in conjunction with Alq<sub>3</sub> showed a maximum luminescence of 10 300 cd m<sup>-2</sup> at 11 V. The nonplanar 9,9-bis(4-phenylamino)fluorene is suggested to be an effective core molecule to make amorphous molecules for OLEDs by the solution process.

The preparation methods of the thin films would affect the charge injection from electrodes and hence the performance of OLEDs, depending upon the kind of materials. Devices using spin-coated films of TPD or *p*-BPD as a hole-transport layer and vapor-deposited Alq<sub>3</sub> as an emitting layer sandwiched between the ITO and Mg : Ag electrodes exhibited higher injected current density and higher luminance than the corresponding devices using vacuum deposited films of TPD or *p*-BPD. On the other hand, no such behavior was observed for the thin films of m-MTDATA or 2-TNATA.<sup>37,48</sup>

### 3.2 Electron-transporting materials

The electron-transporting layer plays the roles of facilitating electron injection from the cathode into the organic layer,

transporting electrons, and blocking holes into the cathode. Consequently, electron-transporting materials should have electron-accepting moieties to form stable anion radicals. Fig. 4 shows the chemical structures of some solution processible electron-transporting materials.

Oxadiazole derivatives, such as 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), have been widely used as ETL in OLEDs. However, PBD is a crystalline material and PBD film tends to recrystallize even at room temperatures. In an attempt to synthesize amorphous materials which form stable glasses, a variety of spiro and branched derivatives of PBD as well as a starburst-dendrimer have been synthesized and suggested as electron transport and hole blocking materials for electrooptical applications.

Triazoles and benzimidazole derivatives are other interesting classes of electron deficient thermostable materials similar to oxadiazoles, *e.g.*, 3-(biphenyl-4-yl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ) and TPBI, which are not only better ETL but also better HBL than PBD. An interesting feature of TPBI is the high solubility in alcoholic solvents, making it suitable for multilayer devices by successive solution processes.<sup>28</sup> Nomura *et al.* reported new amorphous electron-transporting materials 1,3,5-tris[1-(phenoxyphenyl)-1*H*-benzimidazol-2-yl]-benzene.<sup>49</sup> These phenoxy-TPBI showed high thermal stability ( $T_g = 108$ – $110$  °C) and good solubility in common organic solvents, such as acetone, 2-methoxyetanol, tetrahydrofuran, chloroform, and 2-butanone. Pinhole-free transparent films were obtained by spin-casting the 2-butanone solution. The two-layer device with a structure of ITO/T-Caz/*m*-phenoxy-TPBI: 10 wt% DPA/LiF/Al showed a blue emission (35 cd m<sup>-2</sup>) from 9,10-diphenylanthracene (DPA). Fortunately, *m*-phenoxy-TPBI are soluble in 2-butanone and T-Caz as a hole-transporting material is insoluble in 2-butanone. Therefore, multi-layer device might be fabricated by spin cast technique.

Pyridine is also a well-studied electron-deficient heterocycle, pyridine derivatives are promising electron transporting materials for OLEDs.<sup>50</sup> An electron mobility up to  $7.9 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> has been reported for 1,3,5-tri(*m*-pyrid-3-ylphenyl) benzene

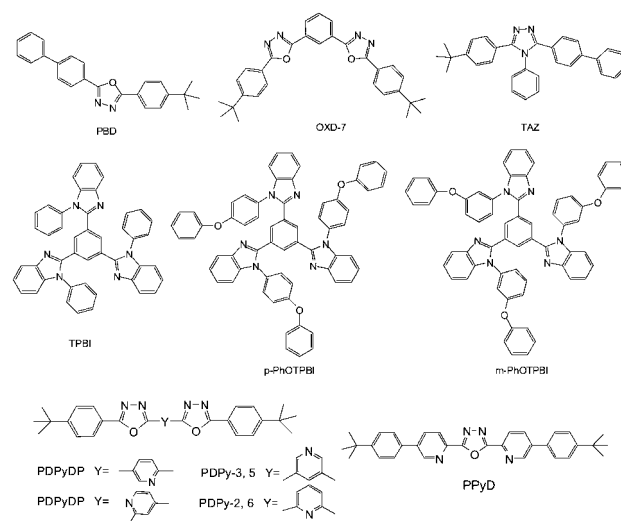


Fig. 4 Molecular structures of electron-transporting materials.

(TmPyPB), which is the highest data ever reported for amorphous molecular materials.<sup>51</sup> Bryce *et al.* designed some soluble pyridine and oxadiazole hybrids.<sup>52–55</sup> They found that single blended-layer devices using 20% of the 1,3,4-oxadiazole-pyridine hybrids and an orange-emitting polymer showed improved external quantum efficiencies.

Although many amorphous electron-transporting materials can be easily dissolved in common organic solvents and form smooth, unique and stable film by wet process, most of the electron-transporting layers are prepared by vacuum deposition to prevent the underlying emitting layer from being redissolved. So *et al.* evaporated a thin PBD layer between the solution processed EML with Ir(mppy)<sub>3</sub> as the dopant, and the CsF/Al cathode.<sup>56</sup> The PBD layer with a LUMO of 2.4 eV is ideally suited to inject charges into the electron manifold comprising both PBD and Ir(mppy)<sub>3</sub> in the EML. The device efficiency was enhanced greatly enhanced to 55 cd A<sup>-1</sup>.

### 3.3 Fluorescent materials

Alq<sub>3</sub> is widely used as an ETL and a green EML in OLEDs since the first report on double-layered OLEDs in 1987 by Tang *et al.*<sup>1</sup> It is interesting to study its solution processability. Kim *et al.* fabricated solution-based formation of multilayers of small molecules with the structure of ITO/PEDOT:PSS/NPB/Alq<sub>3</sub>/LiF/Al fabricated by a direct transfer technique using a mold.<sup>30</sup> The approach involves dissolving a small molecule organic in a solvent, spin coating it on a mold, and then transferring the layer onto the existing organic layer on a substrate. The PEDOT:PSS and NPB layers can be direct spin coated onto the ITO coated glass substrate one by one. The Alq<sub>3</sub> layer spin coated from chloroform onto a poly(urethaneacrylate) mold was transferred to the NPB layer after drying. The maximum luminance of the devices fabricated by this transfer technology ranged from 50% to 90% of that of the device made by the usual evaporation method.

Nevertheless, the film quality of Alq<sub>3</sub> by solution process is not as good as that by vacuum deposition. Recently, many derivatives of Alq<sub>3</sub> have been investigated as emitter materials to fulfill the requirement for solution process, including those with substitution of the metal ion with other metals and substitution of the 8-quinolinol ligand and introduction of other ligands. Fig. 5 shows the chemical structures of some solution processible Al complexes.

Chen *et al.* discovered a new type of small molecular host material based on aluminium(III) 8-hydroxyquinolates with *N*-ethylanilinesulfonamide substituents, abbreviated as Al(Saq)<sub>3</sub> for fabrication of OLEDs using spin-coating techniques.<sup>32</sup> The complex is soluble in commercially available solvents such as 1,2-dichloroethane, THF, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Thin film phase prepared by spin-coating is smooth and pinhole free. To understand the mechanism of thin film formation of Al(Saq)<sub>3</sub>, molecular packing from X-ray was investigated. Because of the hooklike nature of sulfonamide group at C-5, the molecules of Al(Saq)<sub>3</sub> are randomly dispersed in the solvent matrix. The intermolecular hook-like sulfonamide groups are tangled physically and form physical bonding. Therefore, thin film phase could be formed well *via* spin coating. Because of the low density of the packing of phenyl rings in the globular complex, crystallization of Al(Saq)<sub>3</sub> by intermolecular

phenyl ring packing is difficult when the film is spin-coated on the substrate. A single layered device with the structure of glass/ITO (20 nm)/PEDOT:PSS(70 nm)/Al(Saq)<sub>3</sub>(70nm)/LiF(1 nm)/Al(200 nm) initially produced a navy blue emission of CIE<sub>x,y</sub> (0.21, 0.41) with a relatively low luminance efficiency. When doped with 0.7 wt% of a high fluorescent green dopant 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo-[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one (C545T), energy transfer from Al(Saq)<sub>3</sub> to C545T occurs and bright green light emission can be achieved. This new six-coordinated aluminium quinolate with sulfonate substituents can be used as wide band gap host materials ( $E_g \sim 2.9$  eV) for various singlet dopants to tune the emission and efficiency of OLEDs.

Mishra *et al.* synthesized a family of new soluble Alq<sub>3</sub> derivatised at the 5-position of 8-hydroxyquinoline ligand, which were designed to improve solubility in organic solvents and to retain the beneficial spectroscopic and luminescence properties.<sup>57,58</sup> The ligands have alkyl or aromatic groups attached at the 5-position through an –OCH<sub>2</sub>– or –NCH<sub>2</sub>– as the link. The –CH<sub>2</sub>– group ensured minimal effects on the aromatic properties of the ligands, irrespective of the group substituted. These derivatives can be easily spin-coated onto glass and other substrates of desirable thickness. These aluminium complexes showed green luminescence in the range 527–540 nm, similar to Alq<sub>3</sub>. Park *et al.* also designed and successfully synthesized an alkylated aluminium quinoline derivative, tris(4-tridecyl-8-quinolinolato)aluminium (TDALQ), which is highly soluble in chloroform as well as in many other organic solvents to obtain a transparent thin film by spin-casting, representing an emitting material for solution-processable OLEDs.<sup>59</sup> Although fluorescence quantum yields of these derivatives are slightly less than Alq<sub>3</sub>, the improved solubility of these compounds in organic solvents and formation of good quality transparent films made them useful for solution processable OLEDs.

Qiu *et al.* reported metal(III) chelates based on tridentate Schiff base ligands, which have proved to be of high luminescence.<sup>33</sup> The reported metal chelates provide evaporated films with reduced pinhole and roughness comparing with Alq<sub>3</sub>. They discovered a binuclear aluminium chelate with mixed ligands of  $\beta$ -diketone and the tridentate Schiff base, [Al(saph)DPM]<sub>2</sub>

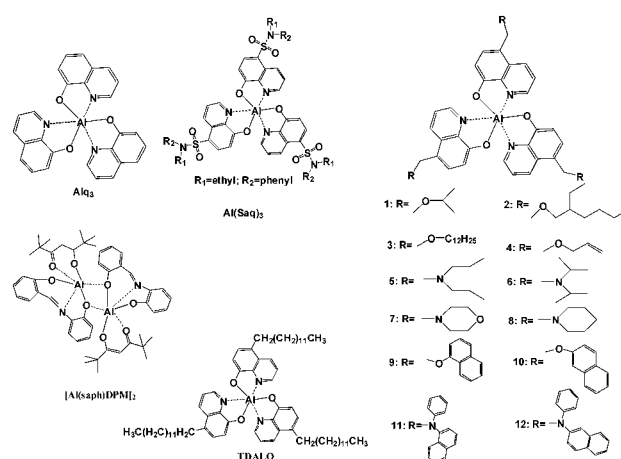


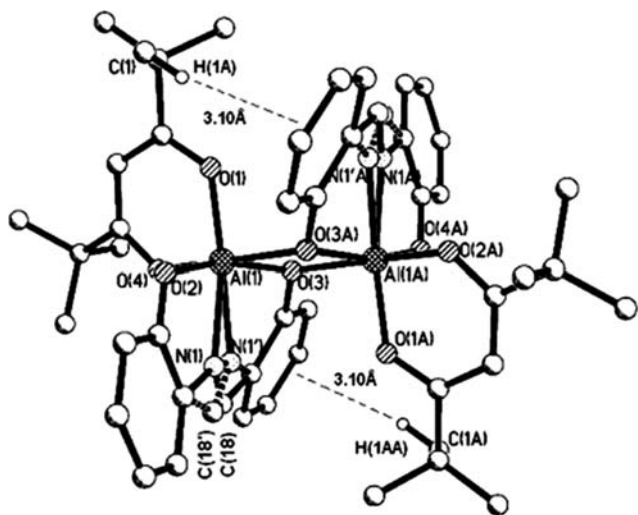
Fig. 5 Molecular structures of fluorescent Al complexes.

bis[(salicylidene-o-aminophenolato)-(dipivaloylmethane)aluminum(III)], which possesses a particular molecular structure and polymer-like molecular packing and solution-processability, that is very different from conventional metal chelates of this type.  $[\text{Al}(\text{saph})\text{DPM}]_2$  was prepared through a complexing reaction in the ethanol solution of  $\text{AlCl}_3$ , saph (salicylidene-o-aminophenol), and DPM (dipivaloylmethane) at a 1 : 1 : 1 molar ratio. Interesting packing and intermolecular interactions have been observed in the crystal lattice

There are two different interactions between the neighboring molecules (Fig. 6). One is the moderate  $\pi$ - $\pi$  stacking interaction, which occurs between the phenyl/phenyl rings of saph ligands. Such  $\pi$ - $\pi$  links generate an extended one-dimensional chain along the b direction. The other is the C-H... $\pi$  intermolecular interactions between the t-butyl groups of one molecule and the phenyl rings of the neighboring one, leading to an aggregation of the hook-like t-butyl groups pointing toward each other. This C-H... $\pi$  interaction thus interlaces with  $\pi$ - $\pi$  stacking chains, resulting in a packing motif quite similar to the conformation of polymer chains, thus suppressing intermolecular aggregation. This polymer-like packing *via* intermolecular interactions in solid  $[\text{Al}(\text{saph})\text{DPM}]_2$  is conducive to film formation by the solution process.

$[\text{Al}(\text{saph})\text{DPM}]_2$  can be dissolved in tetrahydrofuran (THF) and common alcohols. Although  $\text{Alq}_3$  can also be easily dissolved in organic solvents, it has to be sublimed and cannot be deposited from solution; otherwise the underlying hole transporting layer would redissolve. The only solvents that will not dissolve the triaryl amines layer or PVK are water or common alcohols. In contrast, no matter what method,  $[\text{Al}(\text{saph})\text{DPM}]_2$  could form uniform, good optical quality and pinhole-free films, even through spin-coating from methanol solution.

The quantum efficiency of this emission (0.639 in DMF) is high, and 5.5 times that of  $\text{Alq}_3$ , which should be ascribed to largely minimized non-radiative rates due to the rigid binuclear structure. Two bilayer devices with PVK:TPD (1 : 1 weight) as the hole-transporting layer,  $[\text{Al}(\text{saph})\text{DPM}]_2$  or



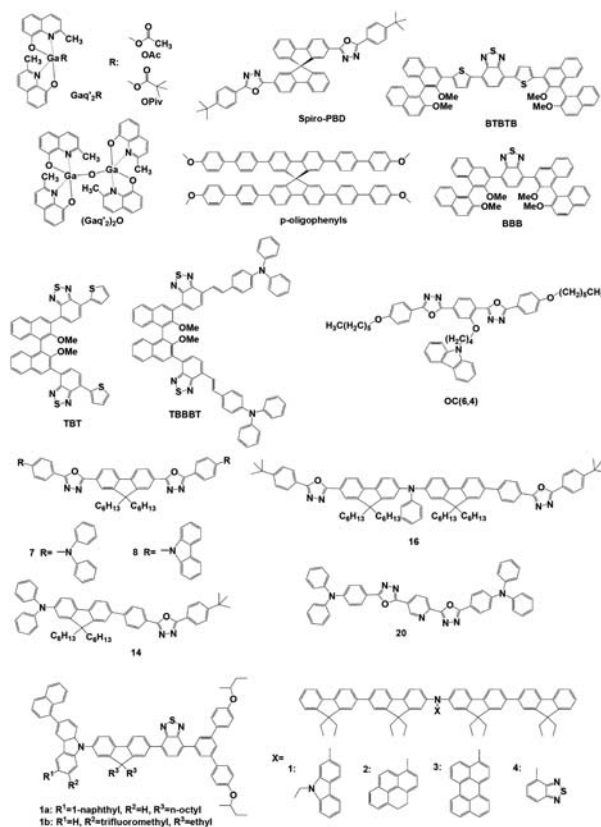
**Fig. 6** The perspective plot of  $[\text{Al}(\text{saph})\text{DPM}]_2$ . The disordered saph is shown by N(1') and C(18') with dashed lines as the bonds to the other atoms. The other hydrogen atoms are omitted for clarity. From ref. 33.

$[\text{Al}(\text{saph})\text{DPM}]_2$ :rubrene (1%) as the emissive layer, were fabricated by successive spin-coating. The undoped device gave strong green emission from  $[\text{Al}(\text{saph})\text{DPM}]_2$  with a maximum brightness of  $2810 \text{ cd m}^{-2}$  at 20 V. The peak efficiency is  $0.5 \text{ cd A}^{-1}$ . The doped device gave the typical emission of rubrene and improved performance. The maximum brightness is  $2900 \text{ cd m}^2$  at 14 V, indicating the efficient energy transfer from  $[\text{Al}(\text{saph})\text{DPM}]_2$  to rubrene. The peak efficiency is  $1.4 \text{ cd A}^{-1}$ .

Elschner *et al.* reported three kind of Ga complexes which can be deposited by spin-coating to substitute  $\text{Alq}_3$ .<sup>25</sup> Ga complexes exhibit high fluorescence quantum yields and their emission spectra are blue-shifted relative to  $\text{Alq}_3$ . The new Ga complexes, abbreviated as  $\text{Gaq}'_2\text{OAc}$ ,  $\text{Gaq}'_2\text{OPiv}$  and  $2(\text{Gaq}'_2)\text{O}$ , can be dissolved in methanol and spin-coated on top of a PEDOT-PSS/TDAPB layer stack, because TDAPB-layer would not dissolve in water or common alcohols. OLEDs fabricated by three subsequently spin-coated layers are presented for the first time, the luminous efficiency of device with  $\text{Gaq}'_2\text{OAc}$  is  $0.39 \text{ cd A}^{-1}$  at  $8 \text{ mA cm}^{-2}$ , which is comparable to those with sublimed emitting layers.

Fluorescent materials other than metal complexes have also been studied, as shown in Fig. 7. Park *et al.* have synthesized N-alkylated carbazole with a variation of alkyl size such as ethyl, hexyl, dodecyl and octadecyl group and have made thin film by using the spin-coating method.<sup>60</sup> Unfortunately, the light intensity of the spin-coated single molecule device is very weak.

Kido *et al.* developed a blue fluorescent fluorene containing arylamine oligomer, bis(9,9,9',9'-tetra-octyl-2,2'-difluorenyl-7-yl)-phenylamine (DFPA).<sup>61</sup> The device exhibited blue emission, the



**Fig. 7** Molecular structures of fluorescent materials.

maximum luminance of 1800 cd m<sup>-2</sup> and an external quantum efficiency of 1.5%. They also designed solution processable bis(di-fluorenyl)amino-substituted carbazole **1**, pyrene **2**, perylene **3**, and benzothiadiazole **4** for OLEDs. The emitting colors can be easily controlled by the central core and they ranged from sky blue to deep red. The outer fluorene oligomers can sterically prevent crystallization and excimer formation between the emitting cores in a neat film. Simple double layer devices based on **1–4** by solution processes showed external quantum efficiencies around 1%.<sup>62</sup>

Li *et al.* studied asymmetrically 4,7-disubstituted benzothiadiazole derivatives (**1a** and **1b**) involving a hole transporting carbazolyl moiety at one end and a solubilizing dendron at the opposite end. A two-layer OLED based on solution-processed **1a** revealed a maximal luminous efficiency of ~10.6 cd A<sup>-1</sup>, which is among the best for non-doped solution-processed fluorescent green OLEDs.<sup>63</sup>

A spiro-linkage is used to modify the steric demand of low molecular organic compounds to improve their processability and morphologic stability. Spiro-linked compounds form stable nonpolymeric organic glasses with high glass transition temperatures, usually associated with amorphous molecules. High quality amorphous films with high morphologic stability can be prepared with these spiro-linked luminescent materials by conventional spin-coating techniques. Salbeck *et al.* presented blue electroluminescence devices with high color purity, high brightness and low turn-on voltage based on these spiro-compounds, *e.g.* spiro-TAD, spiro-MeOTAD, spiro-PBD and spiro-linked *p*-oligophenyls.<sup>41</sup> A blue light-emitting two-layer device, fabricated by combining a hole transporting spiro-TAD with an electron transporting spiro-PBD, shows a turn-on voltage at 2.7 V and a luminance of 500 cd m<sup>-2</sup> at 5 V.

Li *et al.* reported four binaphthyl containing molecules with good solubility, amorphous film-forming ability and high photoluminescence quantum efficiencies: green-emitting BBB and TBT as well as red-emitting BTBTB and TBBBT.<sup>64</sup> The non-planar binaphthyl moiety is presented as a way of reducing intermolecular interactions and help to decrease intermolecular interactions in the film state, and thus result in amorphous materials. The OLED based on BTBTB, showed a turn-on voltage of 2.2 V, a maximum luminance of 8315 cd m<sup>-2</sup>, and a maximum luminescence efficiency of 1.95 cd A<sup>-1</sup>.

To balance carrier injection from electrodes into the emitting layer, multilayer OLEDs with solution-processed small molecules as the EML were fabricated. Nguyen *et al.* presented blue OLEDs using the solution processable small molecule 2,7-dipyrenyl-9,9-dioctyl-fluorene (DPF) as the light-emitting material and conjugated polyelectrolytes as electron injection layers.<sup>65</sup> Blue OLEDs were fabricated using two simple structures: ITO/PEDOT:PSS/DPF/LiF/Al and ITO/PEDOT:PSS/DPF/PFN-BIm<sub>4</sub>/Al, where PFN-BIm<sub>4</sub> is poly[9,9-bis[6'-(*N,N,N*-trimethylammonium)hexyl]fluorene-*alt-co*-phenylene] with tetrakis(imidazolyl) borate counterions. Both device structures show efficient blue light emission from the amorphous DPF film. The device using spin cast PFN-BIm<sub>4</sub> as EIL has a turn-on voltage of 3.8 V, a luminance of 2000 cd m<sup>-2</sup>, and an efficiency of 0.6 cd A<sup>-1</sup>. Using the PFN-BIm<sub>4</sub> layer shows a significant improvement of the device performance when compared to the LiF layer.

For fabricating OLEDs, the presence of very thin layers of both hole-transporting and electron-transporting molecules are

usually required. In several reports on solution-processed OLEDs based on small molecules the authors chemically tailored functional molecules for balanced charge-injection and charge-transport to prepare single-layer devices, which avoids any segregation and suppresses crystallization occurring in active layers consisting of blends of different molecules. Moreover, the chemical linkage may be chosen in order to tailor solubility, morphology and other properties of the active molecules. Neitzert *et al.* reported blue emitting OLEDs with spin-coated small molecule active layer, where an oxadiazole group as electron conductor and light emitter and a carbazole group as hole conductor in a single molecule.<sup>66,67</sup> Taking advantage of the steric constraints due to the side insertion of carbazole unit to the oxadiazole moiety, the compounds are very soluble in chlorinate organic solvents and they can be easily processed to homogenous films. The device with the structure of ITO/PEDOT/OC(6,4)/Al showed the luminous efficacy of 0.06 lm W<sup>-1</sup> at 15 V. The initial degradation of oxadiazole based blue OLEDs was also discussed. Bryce *et al.* designed the new compounds which comprise varying juxtapositions of OXD, fluorene and triphenylamine units along with a related bipolar bis(oxadiazolyl)pyridine system. The simple single-layer device ITO/PEDOT-PSS/X (X = 7, 8, 14, 16, 20)/Ca/Al fabricated using simple spin-coating shows the maximum current efficiency of 1.00 cd A<sup>-1</sup> and power efficiency of 0.56 lm W<sup>-1</sup> at 5.7 V.<sup>24</sup> In particular, the color of the emitted light is tuned from light blue through to green.

High-efficiency solution processable single-layer OLEDs can be obtained from mixed EML,<sup>39</sup> wherein dyes with high quantum efficiency of fluorescence, are doped into a solution processable host with charge-transporting ability. Ohmori *et al.* presented fluorescent OLEDs with TDAPB used as the hole-transporting host material for rubrene fabricated by solution-process.<sup>68</sup> The device structure is ITO/PEDOT:PSS/TDAPB:72wt% PBD:0.3 mol% rubrene/Cs/Al. The luminance of about 10 000 cd m<sup>-2</sup> at 9.2 V and the maximum luminous efficiency of 5.5 cd A<sup>-1</sup> have been achieved.

White emission can be obtained from doping of several fluorophors or phosphors in a single emissive layer. Typically, better composition control over the various dyes is highly easy in the solution process. Pisignano *et al.* described the single-active-layer OLEDs, realized by spin-coating, exhibit good EL performance from red to blue, including balanced white, by tuning blends of different concentrations of a novel functionalized thiophene-based oligomer and a low-molar-mass diamine derivative TPD.<sup>69</sup> In particular, the white-emitting device shows an EL efficiency of 0.5 cd A<sup>-1</sup> and a luminance of more than 180 cd m<sup>-2</sup>. Wang *et al.* investigated OLEDs with spin-coated NPB and 4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl (DPVBi) as the mixed-host, and rubrene and 4,4'-bis(2-(4-(*N,N*-diphenylamino) phenyl)vinyl) biphenyl (DPAVBi) as the dopants. By optimizing the ratios of the components in the EML, they achieved a high efficiency of 8.3 cd A<sup>-1</sup> at 1000 cd m<sup>-2</sup>, which was even better than the evaporated control device with the same device structure.<sup>70</sup>

### 3.4 Phosphorescent materials

To further improve the performance of the solution-processed small molecular OLEDs, solution-processed OLEDs based on phosphorescent dyes (PHOLEDs) doped into soluble hosts have



also been investigated because of their harvesting singlet and triplet excitons, suggesting the potential for approaching a maximum external quantum efficiency of nearly 100%.<sup>71</sup> In PHOLEDs, the triplet emitters are normally used as emitting guests doped into a host material to reduce the concentration quenching and triplet-triplet annihilation. The phosphorescence from the device can be understood in terms of the energy transfer from both the singlet and triplet states of the host molecules to the triplet states of the phosphorescent guest molecules and/or by direct excitation of the phosphorescent guest molecules followed by charge trapping. To simplify the fabrication techniques process, much research effort has been devoted to develop PHOLEDs with the emitting layer prepared by solution-processing recently, wherein the emitters are very often mixed with a soluble host and suitable phosphor in the past several years.

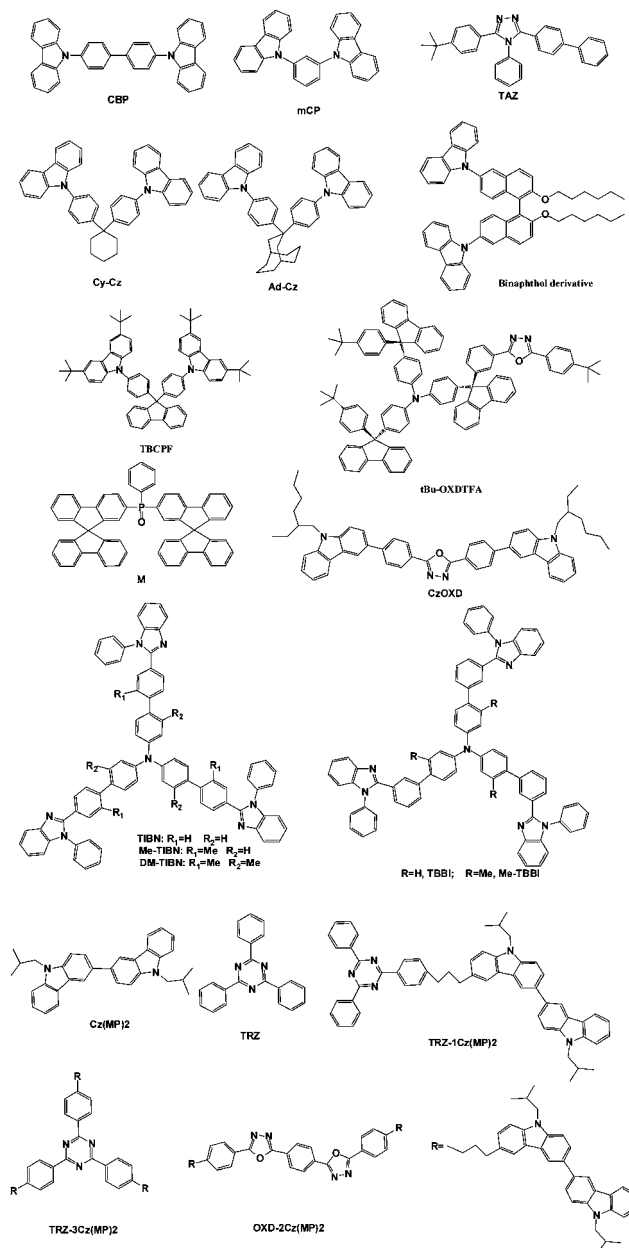
**3.4.1 Hosts for PHOLEDs.** To achieve high efficiencies, the search of suitable host materials for the emissive dopant is of crucial importance for the energy transfer from host to dopant. In order to achieve high device performances, host materials with suitable triplet levels are needed to realize efficient energy transfer from the host to the dopants, and prevent back energy transfer.

Fig. 8 shows the chemical structures of some solution processible host materials. Carbazole and/or triphenylamine derivatives are generally used as the host in PHOLEDs for their relatively high triplet energy and moderate hole-transport ability, e.g., 4,4'-N,N-dicarbazolebiphenyl (CBP), N,N'-dicarbazolyl-3,5-benzene (mCP), TCTA, TDAPB. Triazole derivative 3-(4-Biphenyl)-4-phenyl-5-*tert*-butylphenyl-1,2,4-triazole (TAZ) can be also used as the host with electron-transport ability. Generally, they could form good amorphous films because of their relatively high glass transition temperature.

Triplet energy of CBP ( $T_1$  energy = 2.53 eV) is lower than that of blue-phosphor (e.g., FIrpic,  $T_1$  energy = 2.62 eV), therefore poor energy transfer from CBP to blue-phosphor but rather a back energy transfer process can be observed, which indicates that higher efficiency cannot be attained from this doped system. mCP is shown in the literature to have a  $T_1$  energy of 2.91 eV, which is considerably higher and should therefore prevent undesired back energy transfer from blue-phosphor. Jou *et al.* presented highly efficient WOLEDs by forming therein *via* spin-coating a single white emission layer, in which the red, green, and blue dyes of iridium-based complexes were previously solution-mixed into the host matrix composed of small molecules instead of polymers.<sup>72</sup> Among the small-molecule hosts (CBP, TCTA, mCP and TAZ) studied, the CBP-based devices performed best in terms of luminance and efficiency. The device having a pure white emission of (0.34, 0.35) had a maximum power efficiency of 2.9 lm/W, while 5.6 lm/W at 550 cd m<sup>-2</sup> for that of (0.34, 0.39), which are attributed to have the lowest-energy barrier for electrons to inject from the hole-blocking layer to the host layer.

Recently, several small molecule-based PHOLEDs fabricated with a solution process have been reported based on CBP as a host material doped with different green-, yellow-, and red-phosphors. Additional hole-blocking/electron-transporting layers by thermal vapor deposition were generally used to achieve high efficiency in these papers.<sup>72-78</sup>

However, CBP is far from an ideal host. It has a distinct  $T_c$  of 199 °C, which indicates its crystallization nature.<sup>12</sup> To improve the device performance, new small-molecule hosts were design for solution-processed PHOLEDs. Watanabe *et al.* introduced cyclohexanyl or adamantyl groups between two phenyl rings of CBP (abbreviated as Cy-Cz, Ad-Cz) to improve thermal stability and electron injection.<sup>79</sup> The device with Cy-Cz host material and a green emitting guest Ir(ppy)<sub>3</sub> concentration of 24 wt% showed an external quantum efficiency of 11% and a power efficiency of 27 m W<sup>-1</sup> at 100 cd m<sup>-2</sup>. Gong *et al.* reported small-molecules-based OLEDs using a binaphthol derivative as host and red-emitting Ir(HFP)<sub>3</sub> as guest by a solution process, achieving a maximum luminous efficiency of 0.88 cd A<sup>-1</sup> for single layer devices and of 2.47 cd A<sup>-1</sup> for double layer devices with an electron-transporting layer Alq<sub>3</sub> by thermal vapor deposition.<sup>80</sup>



**Fig. 8** Molecular structures of host materials.

Of the few highly efficient solution-processed OLEDs reported, most devices were investigated with one or more thermal evaporation layers to achieve better balance of charge transport. On the other hand, to balance the charge recombination efficiency, one promising strategy is to mix the hole- and electron-transporting host materials. For example, Kim *et al.* demonstrated a very high efficiency from the solution processed electrophosphorescent OLEDs utilizing small molecular TPBI and NPB doped with red emitter Ir(piq)<sub>3</sub>.<sup>12</sup> The maximum luminous efficiency reached 12.7 cd A<sup>-1</sup>, with its emission peak wavelength of 620 nm. Good performance which was comparable with that of the similar vacuum deposited OLEDs, may be due to the appropriate combination of host molecules with proper energy levels, mobilities, and film forming properties. Ohmori *et al.* selected TDAPB and PBD for single-layer PHOLEDs based on wet processing.<sup>81–84</sup> TDAPB possesses good hole-transport characteristics and the expectation of high triplet energy levels due to the high highest unoccupied molecular orbital (HOMO) levels. In addition, TDAPB resists crystallization due to its steric hindrance and because of its high glass-transition temperature. Furthermore, the mixture system will inhibit the crystallization of PBD, and excellent film forming properties using wet-processing such as spin-coating could be achieved. They studied two types of solution-processed single-layer PHOLED based TDAPB as the host doped with two iridium complexes as dopants, *fac*-tris(2-phenylpyridine) iridium (Ir(ppy)<sub>3</sub>) and tris(1-phenylisoquinoline)iridium(III) (Ir(piq)<sub>3</sub>) for green-emitting and red-emitting phosphorescent materials, respectively. The structures of the devices are as follow: ITO/PEDOT:PSS/emitting layer/Cs/Al. The emitting layer which consisted of the host TDAPB, dopants and an electron-transport material PBD were dissolved in 1,2-dichloroethane. By optimizing the ratios of the various materials, the external quantum efficiency of 8.2% and power efficiency of 17.3 lm/W for green emitting, and 6.3%, 3.0 lm/W for red were achieved. The high performance for the simple device structure may be attributed to excellent film forming properties of the material and efficient energy transfer from the host to dopants.

Recently, Qiu *et al.* designed and synthesized a fluorene/carbazole hybrid 9,9-bis[4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl]fluorene (TBCPF),<sup>85</sup> which has a higher triplet energy ( $T_1$  energy = 2.88 eV) than that of the commonly used blue phosphorescent dye, such as FIrpic. TBCPF with sterically bulky *tert*-butyl groups does not only suppress the self-quenching effect in blue PHOLEDs, but also improves its solubility in common organic solvents, and therefore allows for the formation of homogeneous films by spin-coating. They presented new type of PHOLEDs employing FIrpic doped into TBCPF/OXD-7 co-host matrix. The devices were fabricated by spin-coating a single active layer followed by vacuum deposited a Cs<sub>2</sub>CO<sub>3</sub>/Al cathode. By optimizing the parameters of the single active layer devices, a maximum luminance efficiency of 12.7 cd A<sup>-1</sup> at 190 A m<sup>-2</sup> and brightness of 23 000 cd m<sup>-2</sup> at 20 V were achieved.<sup>86</sup>

Some electron transporting host materials were introduced into small-molecules-based OLED. By using ET host materials, the recombination zone can be confined to the HTL/EML interface, and additional HBL and ETL are no longer necessary. Meerholz *et al.* report on highly efficient PHOLEDs based on

a low-molecular weight electron-conducting host of bis(9,9-spirofluorene-2-yl)-phenylphosphaneoxide (M) doped with *fac*-tris(2-(3-*p*-xylyl)phenyl)pyridine iridium(III) (TEG).<sup>26</sup> All organic layers were spin coated and a strong improvement of performance was achieved by introduction of a hole-transporting double layer based on cross-linkable low-molecular weight molecules. Maximum luminous and power efficiencies of 59 cd A<sup>-1</sup> and 58 lm/W, respectively, are obtained, combined with a low driving voltage and high efficiencies even at high brightness.

Bipolar molecules bearing both electron and hole transporting moieties have attracted considerable interest because their ability to transfer holes and electrons simultaneously. The simplified devices with double-layer or even single-layer structure could be thereby attained based on bipolar materials. By combining suitable electron-rich and -deficient moieties into a molecular structure, several solution-processed bipolar host materials have been synthesized. Kakimoto *et al.* presented a new series of star-shaped bipolar host molecules bearing both hole-transporting triphenylamine and electron-transporting benzimidazole moieties.<sup>87,88</sup> They all exhibit good solubility in common solvents due to the metastructured and star-shaped configuration allowing a solution processing. PHOLEDs based on these bipolar hosts doped with guest Ir(ppy)<sub>3</sub> were fabricated by spin coating technique, which exhibited superior luminance efficiency.

By comprising an electron-rich triphenylamine core and electron-deficient oxadiazole/fluorene peripheries, a solution-processable bipolar material tBu-OXDFTA was synthesized by Chi *et al.*<sup>89</sup> This dendrimer-like molecule not only possesses a high triplet energy (2.74 eV) but also exhibits excellent film-forming properties upon solution processing. Highly efficient white emitting (22.3 cd A<sup>-1</sup>, 11.6%) were obtained from a single white emitting layer formed after spin-coating a solution of blue- and red-phosphor co-dopants containing tBu-OXDFTA as the host matrix.

Ma *et al.* described a bipolar transport compound incorporating both electron- and hole-transport functionalities, namely 2,5-bis(4-(9-(2-ethylhexyl)-9H-carbazol-3-yl)phenyl)-1,3,4-oxadiazole (CzOXD).<sup>90</sup> Smooth and homogeneous films can be obtained by spin-coating from a chloroform solution of CzOXD/iridium complex blends. With the device structure of ITO/PEDOT:PSS/Ir complex:CzOXD/BCP/Alq<sub>3</sub>/LiF/Al, a maximum luminance of 15 232 cd m<sup>-2</sup> and current efficiency of 20 cd A<sup>-1</sup> for a yellow-emitting OLED, and 4896 cd m<sup>-2</sup>, 4.6 cd A<sup>-1</sup> for a red-emitting OLED were achieved.

By incorporating hole and electron-transporting moieties with flexible linkages, Chen *et al.* synthesized nonconjugated bipolar hybrids and demonstrated their potential use as host materials for solution-processed phosphorescent OLEDs.<sup>91</sup> These materials have the potential for solution processing and for the formation of thin films with superior stability against phase separation and thermally activated crystallization. They fabricated OLEDs with the following structures: ITO/MoO<sub>3</sub> (10 nm, thermal evaporation)/EML (40–50 nm, spin-coating)/TPBI(30 nm, thermal evaporation)/CsF (1 nm)/Al (100 nm), in which the emitting layer is of Ir(mppy)<sub>3</sub> doped Cz(MP)<sub>2</sub>, TRZ-3Cz(MP)<sub>2</sub>, or TRZ-1Cz(MP)<sub>2</sub>. The current efficiencies of OLEDs reached a maximum of 32 cd A<sup>-1</sup> for TRZ-3Cz(MP)<sub>2</sub> and the driving voltage decreased monotonically with an

increasing TRZ content, suggesting improved electron injection from the adjacent TPBI layer into the emitting layer.

**3.4.2 Phosphorescent dopants.** Cyclometalated iridium(III) and Pt(II) complexes with organic ligands can show strong triplet emission at room temperature with high quantum efficiency. By changing of the cyclometalated ligands and/or ancillary ligands, the emission colors of these complexes can be tuned over the visible spectrum. Fortunately, most of the Iridium complexes originally designed for vacuum deposition, such as FIrpic for blue, Ir(ppy)<sub>3</sub>, Ir(mppy)<sub>3</sub> for green and Ir(piq)<sub>3</sub>, Ir(piq)<sub>2</sub>acac for red, can be successfully used in solution-processed devices with high efficiency. Fig. 9 shows the chemical structures of some solution processible phosphorescent dopants.

One of the motivations to modify the Iridium complexes for the solution process is to improve their solubility. For PHOLEDs, a high doping concentration of the phosphorescent dopant is required to efficiently harvest the triplet excitons generated on the host. Ir(ppy)<sub>3</sub>, though widely used in vacuum evaporated green PHOLEDs, has a low solubility in common

solvents such as toluene, THF, dichloromethane, chloroform, and chlorobenzene. This low solubility is insufficient for fabrication of Ir(ppy)<sub>3</sub> with the optimum doping levels in the host by solution process. By adding one more xylyl group on each ligand, the resulting molecule of *fac*-tris(2-(3-p-xylyl)phenyl)pyridine iridium(III) (TEG) showed excellent solubility in common organic solvent.<sup>26</sup> Lu *et al.* also reported *tert*-butyl modified iridium complexes for high performance OLEDs by solution process.<sup>92</sup> The resulting complexes of bis(4-*tert*-butyl-2-phenylbenzothiazolato-N,C<sup>2'</sup>) iridium(III)(acetylacetonate) ((*tbt*)<sub>2</sub>Ir(acac)) and bis(4-*tert*-butyl-1-phenyl-1*H*-benzimidazolato-N,C<sup>2'</sup>) iridium(III)(acetylacetonate) ((*tpbi*)<sub>2</sub>Ir(acac)) show excellent thermal stability and high PL quantum efficiencies. The incorporation of the bulky *tert*-butyl substituents into the ligands can also decrease the molecular aggregation and avoid the phase separation.

Meanwhile, the charge balance of electrons and holes is also an important issue for PHOLED research. Along this line, some groups designed multifunctional metallophosphors to improve the charge balance; hence the ambipolar carrier transport together with the favorable triplet energy level alignment between the host material and dopant could be achieved, which will bring about a remarkable enhancement in efficiency. For example, Wong's group designed new series of carbazole- or triphenylamine-based Ir(III) or Pt(II) complexes (Ir-1, Ir-2, Ir-3, Pt-1 and complexes 1–8) recently.<sup>76–78</sup> OLEDs using these complexes as the solution-processed emissive layers have been fabricated, which realize red, orange and white emission with high efficiencies even without the need for the typical hole-transporting layer. In addition, the bulky ligand should also tend to diminish the aggregation of dopants and prevent triplet-triplet annihilation of excitons in at high current density. Yang *et al.* also presented new carbazole-based iridium complexes (Ir(2-PhPyCz)<sub>2</sub>(acac) and Ir(2-PyDeCz)<sub>2</sub>(acac)) used in solution-processable yellow- and red-emitting PHOLEDs.<sup>90</sup> In addition, the long alkyl chain at the N atom of the carbazole was introduced to prevent crystallization and improve the compatibility between the dopants and the host molecules, consequently to suppress the phase separation.

Up to now, most of the studies on solution-processed small molecular electrophosphorescent devices are based on Ir and Pt complexes. However, there are indeed many reports on Re, Os, Eu, and Ru complexes in high-efficiency polymeric OLEDs by solution process.<sup>31,93–96</sup> Therefore, it is expected that these Re, Os, Eu, and Ru complexes can also be used in solution-processed small molecular devices as the phosphorescent dopants.

#### 4. Comparison of solution processed and vacuum deposited small molecules

To further optimize the device performance of solution processed OLEDs, it is important to understand the difference between the films and devices obtained by solution process and vacuum deposition. Fortunately, there are some small molecules which can be used for solution process as well as vacuum deposition. Initial investigations on their differences in morphological, photophysical and electrical properties yield interesting results and may be used as guides for the future researches.

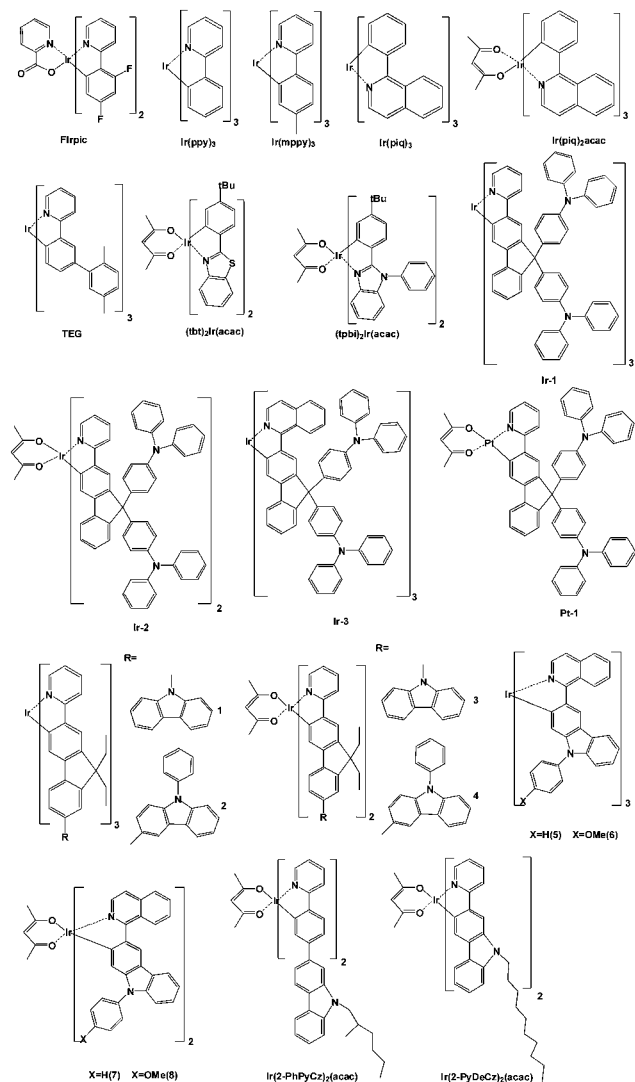


Fig. 9 Molecular structures of phosphorescent dopants.

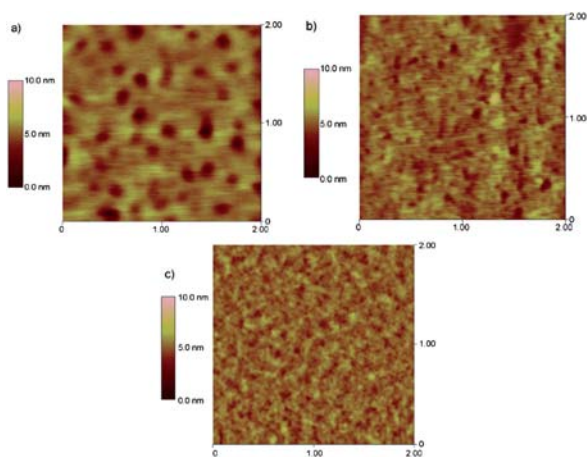
#### 4.1 Film morphology and packing density

Excellent solubility and film forming abilities of the constituting materials are indispensable for solution processed OLEDs. Kim *et al.* investigated the surface morphology of the composite EML films (5 wt% Irpiq<sub>3</sub>: 47.5 wt% NPB: 47.5 wt% TPBI) by spin-coating and vacuum evaporation.<sup>12</sup>

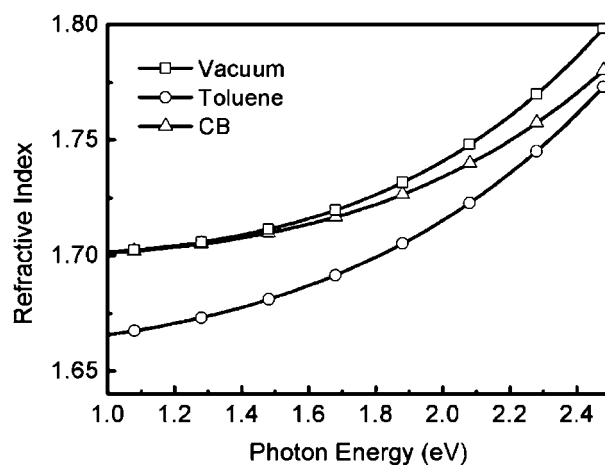
Similar average roughness values of 0.279 and 0.317 nm for vacuum deposited and solution processed films, respectively, were obtained. It demonstrates that a typical amorphous EML film can be fabricated effectively not only by the vacuum deposition process but also by the solution process. The authors attributed the good film forming property of TPBI to the steric hindrance effect imposed by its molecular structure and its high  $T_g$  (124 °C).

They measured the refractive indices of the films and they found that the refractive indices of vacuum deposited film remained higher by about 0.09 than those of solution processed film for the whole wavelength range of the illuminated light (400–1000 nm). Higher refractive index is generally related to higher packing densities. It is clear that the bulk structures of the films showed some inherent differences resulting from the fabrication methods, in spite of similar surface morphologies of the films. Kim *et al.* observed solution process OLEDs based on the composite EML showed higher driving voltage and they attributed this to the lower packing density and then lower mobility in the film.<sup>12</sup>

Lee *et al.* studied the effect of solvents on the morphology of the solution-processed films.<sup>97</sup> They dissolved 5wt% (DPAV-Bi):95wt% 2-(t-butyl)-9,10-bis(2'-naphthyl) anthracene (TBADN) in toluene and chlorobenzene. After spin coating, the films were baked for 15 min (at 100 °C) on a hot plate under N<sub>2</sub> atmosphere. The AFM images of the films are shown in Fig. 10. The root-mean-square (RMS) roughness values of spin-coated films obtained from toluene and chlorobenzene solutions were 0.655 and 0.520 nm, respectively. These values are quite similar to that of a vacuum-deposited film (*i.e.*, 0.575 nm). However, that the film obtained from the toluene solution exhibited a kind



**Fig. 10** AFM images of spin-cast TBADN: DPAVBi films (95w/5w) obtained from (a) toluene, (b) chlorobenzene solutions, and (c) a vacuum-deposited film. From ref. 97.

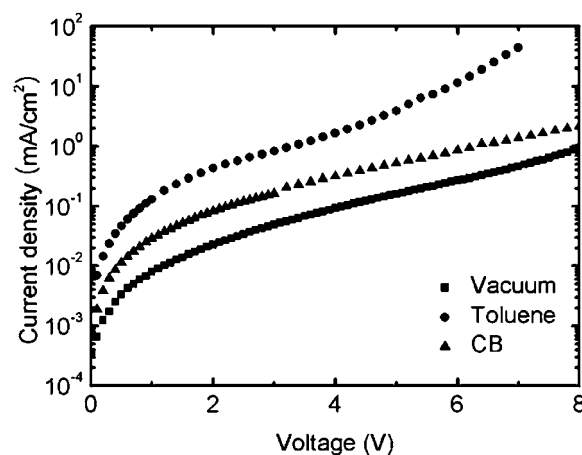


**Fig. 11** Spectroscopic ellipsometry data of solution-processed (toluene and chlorobenzene, CB) and vacuum-deposited TBADN films. From ref. 97.

of aggregation, or phase segregation, which was not observed in the layer obtained from the chlorobenzene solution.

Lee *et al.* also measured the refractive index for the three types of films. As depicted in Fig. 11, the ordinary refractive index of the spin-cast film obtained from the toluene solution is much lower than that of the vacuum-deposited film, which can be attributed to the lower packing density and the presence of free volume inside the former layer. These results agree well with those reported by Kim *et al.* The film obtained from the chlorobenzene solution, however, shows a refractive index that is only slightly below that of the vacuum-deposited film. In this way, the packing density of the solution processed film was successfully tuned by rheology control.

Though the packing densities were lower for spin-coated films, much higher current densities were measured in respective hole-only devices by Lee *et al.*, as shown in Fig. 12. This seems controversial to the results by Kim *et al.* One of the reasons for the high current density in the TBADN film cast from toluene

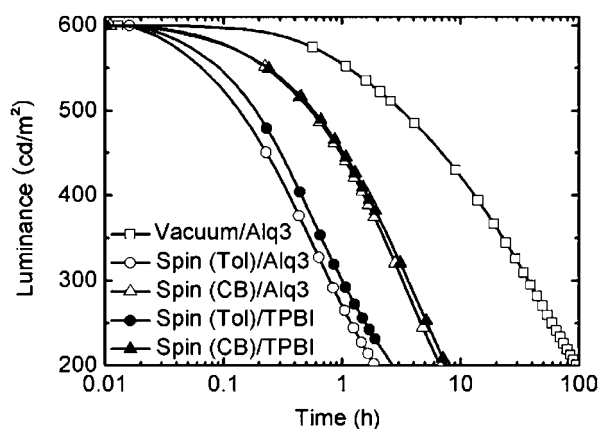


**Fig. 12** Current density versus voltage characteristics of solution-processed (toluene and chlorobenzene, CB) and vacuum-deposited hole-only devices of ITO/PEDOT:PSS/TBADN (130 nm)/Au structure. From ref. 97.

solution is the local molecule aggregation, which provides an efficient charge-transport pathway. Aggregation is not likely to take place during the spin-coating process. In the spin-coating process with a fast rotation rate, most of the solution on the substrate is spun out by the centrifugal force. The remained solvent evaporates quickly. Therefore, molecules in the remained solvent have no enough time to crystallize.<sup>98</sup> However, as the baking temperature of 100 °C is close to the  $T_g$  of TBADN, aggregation is easy to occur.

For display and lighting application, stable OLEDs are required. Though the degradation of vacuum deposited devices have been intensively studied, there are only a few reports on the lifetime of solution processed OLEDs using small molecules. Lee *et al.* studied the stability of the OLEDs with TBADN:DPAVBi as the EML and they found the lifetimes were significantly shorter for the solution-processed devices than for their vacuum-processed counterparts (Fig. 13). OLEDs processed from the chlorobenzene solution showed longer lifetimes than those fabricated from the toluene solution, although the efficiency was lower. The device lifetime showed strongly dependence on the film-processing conditions, regardless of the kind of ETL used (Alq<sub>3</sub> or TPBI). This result indicates that the crucial factor determining the device lifetime is film morphology and the packing density. Since the molecules in the films obtained by solution processing are not as closely packed as those in the vacuum-based layers, solvent impurities may remain inside the solution-processed films and oxygen can diffuse into the film more easily. Lee *et al.* then suggested that the lifetime of solution-processed devices could be improved by controlling the film morphology so as to increase the density of the obtained layers.

Actually, it has been demonstrated possible to adjust the density of the spin-coated films by modification of the solute. By grazing incidence X-ray diffraction, Kakimoto *et al.* measured the film density of spin-coated tris(40-(1-phenyl-1H-benzimidazol-2-yl)biphenyl-4-yl)amine (TIBN) and tris-(2,20-dimethyl-40-1-phenyl-1H-benzimidazol-2-yl)biphenyl-4-yl)yl)biphenyl-4-yl)amine (DM-TIBN).<sup>88</sup> The density of the spin-coated DM-TIBN films (1.08 g cm<sup>-3</sup>) was



**Fig. 13** Luminance decay versus time characteristics of solution-processed (toluene and chlorobenzene, CB) of ITO/PEDOT:PSS/TBADN:DPAVBi/Alq<sub>3</sub>(or TPBI)/LiF/Al structure and vacuum-deposited devices of ITO/PEDOT:PSS/TBADN:DPAVBi/Alq<sub>3</sub>/LiF/Al structure under an electrical current stress (at an initial brightness of 600 cd m<sup>-2</sup>). From ref. 97.

significantly lower than that of the vacuum-deposited film (1.14 g cm<sup>-3</sup>) whereas the densities of spin-coated and vacuum-deposited TIBN films were almost the same, with values of 1.19 and 1.20 g cm<sup>-3</sup>, respectively.<sup>88</sup>

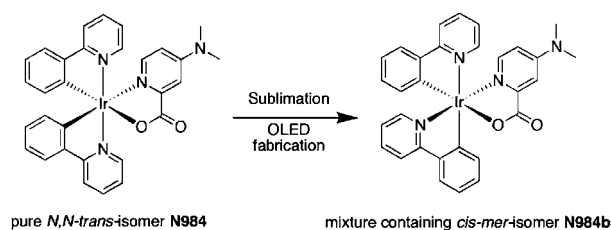
As to OLEDs based on polymeric materials, thermal annealing of the EML has been demonstrated to be effective in improving the device lifetime and has now become a standard procedure for making devices.<sup>99,100</sup> In a very recent report, Wang *et al.* found that by annealing the spin-coated small molecule layer of NPB:DPVBi at 130 °C for 15 min, the lifetime of the solution processed OLED achieved even better lifetime than the evaporated control device with the same structure.<sup>70</sup> Though the annealing temperature they adopted was above the  $T_g$  of either NPB or DPVBi, no crystallization or phase separation was observed. This surprising result may be a good starting point for future research.

In short, stable OLEDs by solution processes can be expected by molecule modifications, process condition optimization, proper thermal treatment and rational design of device structures.

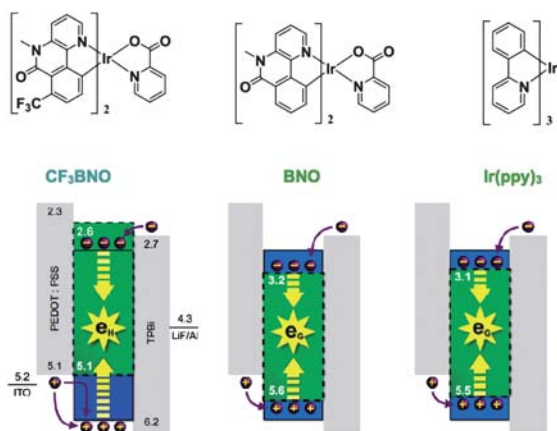
## 4.2 Chemical structure

Beranoff *et al.* reported that sublimation is not an “innocent” technique as thermal isomerization may occur.<sup>101</sup> They observed isomerization of a neutral bis-cyclometalated iridium(III) complex during the preparation of vacuum-processed OLEDs. Isolation of the isomer revealed a *cis* organization of the two pyridine rings of the cyclometalating ligands, as shown in Fig. 14. Photophysical studies showed very similar emission properties of the two isomers. However, it is only possible to prepare vacuum-processed OLED devices having a mixture of isomers due to *in situ* isomerization. They suggested that solution processed devices can have a better purity of the emitter.<sup>101</sup>

For some small molecules with large molecular weight, decomposition during thermal vacuum evaporation is also evident. Jou *et al.* developed two new green iridium complexes, CF<sub>3</sub>BNO and BNO,<sup>102,103</sup> as shown in Fig. 15. The quantum yields were 95%, 42%, and 38% for CF<sub>3</sub>BNO, BNO, and Ir(ppy)<sub>3</sub>, respectively. The high quantum yield of CF<sub>3</sub>BNO should favor the fabrication of a high-efficiency device. However, for OLEDs fabricated by vacuum evaporation, CF<sub>3</sub>BNO and BNO doped devices all showed lower efficiency than the Ir(ppy)<sub>3</sub> doped device. The reason why the vacuum deposited devices had exhibited lower device efficiencies were attributed to their high molecular weights (869 g mol<sup>-1</sup> and 733 g mol<sup>-1</sup> for CF<sub>3</sub>BNO and BNO respectively) and low decomposition temperatures



**Fig. 14** Structure of starting material N984 and of the isomer after sublimation N984b. From ref. 101.



**Fig. 15** Molecular structure of  $\text{CF}_3\text{BNO}$  and  $\text{BNO}$  and the energy diagram of the OLEDs (the device structure is the same for spin coated and vacuum deposited OLEDs). From ref. 103.

(290 °C and 222 °C for  $\text{CF}_3\text{BNO}$  and  $\text{BNO}$  respectively), which would make it difficult to be vacuum-evaporated at elevated temperatures without decomposition. For the devices by spin-coating,  $\text{CF}_3\text{BNO}$  and  $\text{BNO}$  doped devices exhibited extremely high efficiencies of 70.1 lm/W and 39.8 lm/W at the brightness of 100  $\text{cd m}^{-2}$  while the  $\text{Ir}(\text{ppy})_3$  doped device only showed a low efficiency of 18.4 lm/W. They concluded that “large” molecule containing OLEDs can be made with high-efficiency by using solution process.

## 5. Summary and outlook

Solution processed small molecule OLEDs have drawn more and more research attention, as such devices combine the easy synthetic advantages of small molecules with the low-cost solution process. This article has reviewed the device structures adopted to achieve high performance solution processed OLEDs and the small molecules developed for solution process. Recent studies on the difference between the films and devices fabricated by solution process and those by vacuum deposition have been summarized.

To catch up with the state-of-the-art OLEDs fabricated by vacuum deposition, the performance of the solution processed OLEDs still needs to be improved. Although there were some reports about highly efficient and stable OLEDs by solution process, details about the molecular structures and the process conditions have not been fully disclosed.<sup>13,104</sup> In the scientific literature, the best efficiencies of solution processed devices are approaching their evaporated counterparts, while their lifetimes are still orders of magnitude shorter. Initial studies suggested that solution-processed films are less dense than their vacuum-deposited counterparts, which can be a major factor limiting the performance of solution-processed devices.

High performance solution processed OLEDs might require a multiple layer structure with distinct, well-defined interfaces. Optimization of the device structure and process conditions is highly required. The effect of solvent upon the quality of solution processed films needs further investigations. Moreover, phosphorescent small molecules are very sensitive to oxygen and

water, so the environment for the film formation should be carefully controlled.

Alongside the development of new soluble materials, study on the structure–property relationship is of equal importance. It has been demonstrated that incorporation of alkyl or alkoxy groups is useful for enhancing the solubility and the hook-like nature of flexible groups randomly dispersed in the solvent matrix will benefit the formation of amorphous film phase *via* wet processing. Non-planar star-shaped molecules with three or more side-arms also favor the formation of high quality films due to their molecular packing geometry and low crystallinity.

A more challenging task is to develop total solution OLED with printable cathode. By using polymer ETLs compatible with high work function metals, Cao *et al.* successfully demonstrated polymeric OLEDs with conducting Ag paste cathode.<sup>91</sup> This unique technique affords all-printable polymeric OLEDs, and similar strategy could be employed to develop roll-to-roll printed small molecule displays and lighting devices.

There is a long way to go for solution processed OLEDs based on small molecules to fully demonstrate their potentials for ubiquitous and low-cost displays and lightings. However, with the efforts of the researchers devoted to this area, such a dream is within reach.

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