## Journal of Materials Chemistry C

## PAPER

Cite this: J. Mater. Chem. C, 2014, 2, 1104

Received 16th October 2013 Accepted 9th November 2013

DOI: 10.1039/c3tc32024c

www.rsc.org/MaterialsC

### Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) that contain transition-metal complexes, especially iridium(III) complexes, have attracted much attention in recent years because they can fully utilize both singlet and triplet excitons to realize a theoretical internal quantum efficiency of 100%.<sup>1-11</sup> However, most of the high performance PhOLEDs have multilayered device structures fabricated *via* sequential vacuum deposition of small molecules with different functions, which is time-consuming and costly.<sup>12-15</sup> In contrast to thermal evaporation methods, solution-processed techniques

"School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu, 211189, P. R. China. E-mail: 101011462@seu.edu.cn; sun@seu.edu.cn

<sup>b</sup>State Key Lab of Silicon Materials, Zhejiang University, Hangzhou, Zhejiang, 310027, P. R. China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3tc32024c

Wenwen Tian,<sup>a</sup> Chang Yi,<sup>a</sup> Bo Song,<sup>a</sup> Qi Qi,<sup>ab</sup> Wei Jiang,<sup>\*a</sup> Yingping Zheng,<sup>a</sup> Zhengjian Qi<sup>a</sup> and Yueming Sun<sup>\*ab</sup>

The fabrication of electroluminescent devices that combine high device performance with simple device configuration remains an attractive challenge due to their low cost and simple fabrication processes. In this paper, a new series of electrophosphorescent small molecule iridium(III) complexes with diphenylamine-based dendrons of good solubility have been designed. The relationships between their dendritic structures and their photophysical, electrochemical, and electrophosphorescent performances have been systematically investigated. With second-generation dendrons, the photoluminescence quantum yields of the neat film of the dendrimers are almost seven times higher than that of their prototype G0 ( $Ir(LG0)_3$ , LG0 = 1-methyl-2-phenyl-1H-benzimidazole), and three times that of the firstgeneration dendron G1 ( $Ir(LG1)_3$ , LG1 = 4-(1-methyl-1H-benzimidazol-2-yl)-N,N-diphenylbenzenamine). High-quality films of the dendrimers G2 (Ir(LG2)<sub>3</sub>, LG2 = 1-methyl-2-[4-bis[4-(diphenylamino)phenyl]aminophenyl]-1*H*-benzimidazole) and G2Cz ( $Ir(LG2Cz)_3$ , LG2Cz = 1-methyl-2-[4-bis[4-(9-carbazolyl)]-1*H*-benzimidazole) phenyl]-aminophenyl]-1H-benzimidazole) have been fabricated by spin-coating, producing highly efficient, non-doped phosphorescent organic light-emitting diodes (PhOLEDs). With a device structure of indium tin oxide/poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonic acid)/neat dendrimer/  $Cs_2CO_3/Al$ , maximum luminous efficiencies of 14.02 cd A<sup>-1</sup> and 18.35 cd A<sup>-1</sup> have been realized, exhibiting ultrahigh luminous efficiency for single-layer self-host green PhOLEDs. The excellent performances are due to the flower bouquet-shaped iridium dendrimers, which may improve the electron injection and result in greater balance between electron and hole fluxes by the exposure of electron-deficient moieties. The molecular design reported here provides a simple and effective approach to balance charge injection/transporting capacities and develops highly efficient non-doped phosphors suitable for low-cost single-layer device technologies.

> are more promising with respect to the reduction of fabrication cost as well as the realization of large-area displays. Particularly, as the intermiscibility of the interfaces between the upper and lower layers is considered to be a serious problem in multilayered solution-processed devices, it would be more advantageous if both carrier-transporting materials and emissive guests could be integrated into only one active layer.16-20 In view of this, most single-layer devices have been developed containing both hole-transporting and electron-transporting materials as dopants, such as poly(N-vinylcarbazole) (PVK) and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) used in the literature.<sup>19,21-24</sup> Dispersion of the Ir<sup>3+</sup> complex in these host materials not only contributes to charge transport, but also separates the phosphors and avoids self-quenching. Although this technique is usually effective, these doping systems were inferior in phase stability, processability, and repeatability. To overcome these problems, non-doped devices should be fabricated, where the phosphor is utilized as the emitting layer independently.<sup>25-32</sup> Therefore, it is highly



View Article Online

View Journal | View Issue

Self-host homoleptic green iridium dendrimers based on diphenylamine dendrons for highly efficient single-layer PhOLEDs<sup>+</sup>

desirable to develop such self-host phosphors for single-layer devices.

Dendrimers are three-dimensional macromolecules which possess the advantages of the well-defined structures of small molecules together with the good solution processibility of polymers.<sup>33</sup> Moreover, the periphery dendrons can effectively reduce the strong concentration quenching resulting from the interactions of emitting cores. Recently, Burn and co-workers first developed a class of phosphorescent dendrimers composed of an Ir(III) core, meta-bonded phenylene dendrons, and 2-ethylhexyloxy surface groups for good solubility.34,35 However, this usually causes significant reduction in charge mobility.<sup>36,37</sup> Thus, to achieve better charge transport, carbazole-based and triphenylamine-based dendrons are introduced to iridium complexes.38-48 In addition, bipolar iridium dendrimers have been developed by introducing electron-rich and electron-deficient moieties to the molecules.49-51 Unfortunately, despite good performances in multilayered PhOLEDs with these iridium dendrimers as emissive materials, poor performances have been observed for single-layered ones.38,49 The low cost and simple fabrication of electrophosphorescent devices that combine high device performance with simple device configuration remains an attractive challenge.

Hence, herein, in searching for electrophosphorescent iridium complexes with good balanced electron and hole transporting capacities for single-layer devices, we report the synthesis and electroluminescent properties of new, green emitting iridium(III) complexes with diphenylamine-based dendritic ligands up to the second generation. The main advantage of this design can be summarized in several points. Firstly, the high triplet energy of these dendrons can prevent back energy transfer from the emissive Ir core to peripheral dendrons.43,52 Secondly, the complex is surrounded by a branched shell to prevent self-aggregation or concentration quenching of the emissive core in the solid state. Thirdly, the diphenylamine-based dendrons, which display stronger electron donating abilities than their triphenylamine-based and the carbazole-based counterparts, are ideal electron donors with low aggregation tendency, high carrier mobility, and high thermal and photochemical stability.53 Additionally, the dendritic diphenylamine compounds have better solubility in common organic solvents relative to carbazole-based dendrons as a result of increased flexibility.54 Finally, by introducing the dendrons into the para-site of the phenyl segment of the 2-phenylbenzimidazole ligand, flower bouquet-shaped iridium dendrimers have been obtained, which place the benzimidazole moieties on the surface rather than trapped in the center of the molecule. Since the electron clouds of the LUMO levels of dendrimers are largely located on the phenylbenzimidazole moieties according to theoretical calculations,40 the electron injection (EI) characteristics could be greatly improved because of the reduced barrier for the injection of electrons. Coupled with the good hole injection properties afforded by the dendrons, good EI characteristics can ensure excellent EL performance.55

In this work, a dendritic phenyl benzimidazole ligand LG2 and its encapsulated homoleptic Ir(m) complex G2 have been designed and synthesized, along with G0 and G1 for

comparison. The CzDPA dendritic Ir( $\pi$ ) complex G2Cz was also designed to study the effect of increased molecular rigidity as well as maintaining good solubility. The devices from G2 and G2Cz showed maximum luminance efficiencies of 14.02 cd A<sup>-1</sup> and 18.35 cd A<sup>-1</sup> for single-layer self-host devices respectively. To the best of our knowledge, the EL efficiencies enabled by G2 and G2Cz are the highest ever reported for single-layer self-host green emissive devices fabricated by spin-coating. This work should encourage further extensive investigations into the importance of the location of the substituents on the ligands of phosphorescent complexes regarding device characteristics and performance.

## Experimental

#### General information

<sup>1</sup>H-NMR spectra were measured on a BRUKER AMX 300- or 500 MHz instrument with tetramethylsilane as the internal standard. Molecular masses were determined by electrospray ionization-mass spectrometry (ESI-MS) using a FINNIGAN LCQ instrument, or matrix-assisted laser desorption-ionization timeof-flight mass spectrometry (MALDI-TOF-MS) using a BRUKER DALTONICS instrument, with  $\alpha$ -cyano-hydroxycinnamic acid as a matrix. Elemental analyses were performed on a Vario EL III elemental analyzer. Absorption and photoluminescence emission spectra of the target compound were measured using a SHIMADZU UV-2450 spectrophotometer and a HORIBA FLUO-ROMAX-4 spectrophotometer, respectively. The solution PL quantum efficiency was measured by a relative method using  $(ppy)_2$ Ir(acac) ( $\Phi_p = 0.34$  in 2-methyltetrahydrofuran) as the standard in degassed DMSO solutions. The film PL quantum efficiency was measured with an integrating sphere under an excitation wavelength of 370 nm. Phosphorescence spectra at 77 K were measured in a dichloromethane solvent. Phosphorescence lifetime measurements were performed on a HORIBA FM-4P-TCSPC fluorescence spectrometer, with a pulsed 390 nm NANOLED source in degassed DMSO solutions. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449-F3 thermal analyzer under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Cyclic voltammetry (CV) was performed on a CHI750C voltammetric analyzer in CH<sub>2</sub>Cl<sub>2</sub> solutions at a scan rate of 100 mV s<sup>-1</sup> with a glassy carbon rod as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium perchlorate (0.1 M) and ferrocene was selected to determine the potential of the silver wire electrode (0.14 V vs. saturated calomel electrode (SCE)). The solutions were bubbled with a constant nitrogen flow for 15 min before measurements. X-ray diffraction (XRD) was performed on a BRUKER D8-DISCOVER diffractometer using Cu Ka radiation.

#### Quantum chemical calculations

The geometric optimization of the ground state of the complexes was carried out using the Becke-Lee-Yang-Parr composite exchange correlation functional (B3LYP) method.

"Double- $\xi$ " quality basis sets were employed for the C, H and N (6-31G) and the Ir (LANL2DZ).<sup>56</sup> An effective core potential (ECP) replaces the inner core electrons of Ir leaving the outer core  $(5s)^2(5p)^6$  electrons and the  $(5d)^6$  valence electrons of Ir(m). All of the calculations were accomplished with the Gaussian 03 software package *in vacuo* without any constrained symmetry. The molecular orbitals were visualized using Gaussview.

#### Device fabrication and performance measurements

In a general procedure, indium tin oxide (ITO)-coated glass substrates were precleaned carefully and treated by UV ozone for 4 min. A 40 nm poly(3,4-ethylenedioxythiophene) doped with poly(styrene-4-sulfonate) (PEDOT:PSS) aqueous solution was spin coated onto the ITO substrate and baked at 210 °C for 10 min. The substrates were then taken into a nitrogen glove box, where the emitting layer (100 nm) was spin coated onto the PEDOT:PSS layer from 1,2-dichloroethane solution and annealed at 120 °C for 30 min. The substrate was then transferred into an evaporation chamber, where the Cs<sub>2</sub>CO<sub>3</sub>/Al bilayer cathode was evaporated at evaporation rates of 0.2 and 10 Å s  $^{-1}$  for Cs2CO3 and Al, respectively, under a pressure of 1  $\times$  $10^{-3}$  Pa. The current-voltage-brightness characteristics of the devices were characterized with a Keithley 4200 semiconductor characterization system. The electroluminescent spectra were collected with a Photo Research PR705 Spectrophotometer. All measurements of the devices were carried out in an ambient atmosphere without further encapsulation.

#### Materials

All reagents were used as purchased without further purification. All manipulations involving air-sensitive reagents were performed under a dry nitrogen atmosphere. 1-Methyl-2-phenyl-1*H*benzimidazole (**LG0**),<sup>57</sup> 4-(diphenylamino)benzaldehyde (2),<sup>58</sup> 4-[bis[4-(diphenylamino)phenyl] amino]benzaldehyde (5),<sup>59</sup> and 4-[bis[4-(9*H*-carbazol-9-yl)phenyl]amino]benzaldehyde (6)<sup>59</sup> were prepared according to literature procedures.

#### 4-(1H-Benzimidazol-2-yl)-N,N-diphenylbenzenamine (3)

A mixture of 1,2-diaminobenzene (1.30 g, 12.0 mmol), 4-(diphenylamino)benzaldehyde (2.73 g, 10.0 mmol), ammonium chloride (0.54 g, 10.0 mmol), and DMF (40 mL) was heated at 80 °C for 12 h. After cooling to room temperature, the mixture was poured into water for extraction with ethyl acetate. The organic extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent had been removed, the residue was purified by column chromatography on silica gel with petroleum/ethyl acetate (5 : 1) as the eluent to give the product in a yield of 42%. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): 8.03 (d, J = 8.6 Hz, 2H), 7.53 (s, 2H), 7.36 (t, J = 7.8 Hz, 4H), 7.16–7.12 (m, 8H), 7.03 (d, J = 8.6 Hz, 2H).

# 2-[4-Bis[4-(diphenylamino)phenyl]aminophenyl]-1*H*-benzimidazole (7)

This compound was prepared according to the procedure for the synthesis of (3), in a yield of 40%. <sup>1</sup>H NMR (500 MHz, DMSO-

d<sub>6</sub>): 8.02 (d, J = 9.0 Hz, 2H), 7.53 (s, 2H), 7.29 (t, J = 8.0 Hz, 8H), 7.15–6.98 (m, 24H).

# 2-[4-Bis[4-(9*H*-carbazol-9-yl)phenyl]aminophenyl]-1*H*-benzimidazole (8)

This compound was prepared according to the procedure for the synthesis of (3), with a yield of 47%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 12.83 (s, 1H), 8.27–8.20 (m, 6H), 7.66 (d, J = 8.1 Hz, 5H), 7.52–7.41 (m, 15H), 7.32–7.29 (m, 4H), 7.20–7.19 (m, 2H).

## 4-(1-Methyl-1*H*-benzimidazol-2-yl)-*N*,*N*-diphenylbenzenamine (LG1)

4-(1H-Benzimidazol-2-yl)-N,N-diphenylbenzenamine (3.61 g, 10.0 mmol) was dissolved in DMF (80 mL) containing potassium carbonate (3.45 g, 25.0 mmol). The mixture was cooled in an ice bath while iodomethane (1.70 g, 12.0 mmol) was added in a dropwise manner. The reaction was allowed to return to room temperature and stirred for an additional 12 h at which time the reaction mixture was filtered to remove the potassium carbonate. The DMF was removed under reduced pressure and the residue in 100 mL chloroform was washed with water and dried over anhydrous sodium sulfate. After the solvent had been removed, the residue was purified by column chromatography on silica gel with petroleum/ethyl acetate (5:1) as the eluent to give the product in a yield of 72% (2.70 g). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 7.76 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 4H), 7.26-7.13 (m, 8H),7.05 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H). MS (ESI): m/z 376.2 [M + H]<sup>+</sup>.

# 1-Methyl-2-[4-bis[4-(diphenylamino)phenyl]aminophenyl]-1*H*-benzimidazole (LG2)

This compound was prepared according to the procedure for the synthesis of **LG1**, with a yield of 76%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 7.73 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.32–7.17 (m, 11H), 7.12–6.99 (m, 21H), 3.86 (s, 3H). MS (ESI): m/z 710.4 [M + H]<sup>+</sup>.

#### 1-Methyl-2-[4-bis[4-(9H-carbazol-9-yl)phenyl]aminophenyl]-1H-benzimidazole (LG2Cz)

This compound was prepared according to the procedure for the synthesis of **LG1**, with a yield of 84%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 8.26 (d, J = 7.5 Hz, 4H), 7.93 (d, J = 8.7 Hz, 2H), 7.69–7.61 (m, 6H), 7.55–7.41 (m, 14H), 7.33–7.27 (m, 6H), 3.95 (s, 3H). MS (ESI): m/z 706.3 [M + H]<sup>+</sup>.

#### **Dendrimer G0**

A mixture of 1-methyl-2-phenyl-1*H*-benzimidazole (1.1 mmol), iridium chloride trihydrate (0.17 g, 0.5 mmol), 2-ethoxyethanol (10 mL), and water (3 mL) was refluxed under nitrogen for 24 h. The precipitate was collected by filtration, washed with water and ethanol, and then vacuum dried. A mixture of the chlorobridged dimer, 1-methyl-2-phenyl-1*H*-benzimidazole (0.6 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.35 g, 2.5 mmol) in glycerol (30 mL) was heated to 190 °C for 24 h under nitrogen. After cooling to room temperature, the mixture was poured into water for extraction

#### Paper

with dichloromethane. The organic extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent had been removed, the residue was purified by column chromatography on silica gel with petroleum/dichloromethane (2 : 3) as the eluent to give the product in a yield of 17%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 7.85 (d, J = 7.8 Hz, 3H), 7.69 (d, J = 8.1 Hz, 3H), 7.18–7.12 (m, 3H), 6.83–6.78 (m, 3H), 6.71–6.65 (m, 9H), 6.01 (d, J = 7.8 Hz, 3H), 4.26 (s, 9H). MALDI-TOF-MS (m/z): calcd. for C<sub>42</sub>H<sub>33</sub>N<sub>6</sub>Ir: 813.98, found: 813.22. Anal. calcd (%) for C<sub>42</sub>H<sub>33</sub>N<sub>6</sub>Ir: C, 61.97; H, 4.09; N, 10.32. Found: C, 62.02; H, 4.23; N, 10.24.

#### Dendrimer G1

This compound was prepared according to the procedure for the synthesis of **G0**, with a yield of 35%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 7.66 (d, J = 8.1 Hz, 3H), 7.50 (d, J = 8.7 Hz, 3H), 7.20–7.10 (m, 15H), 6.93 (t, J = 7.5 Hz, 6H), 6.74–6.66 (m, 15H), 6.56 (d, J = 2.1 Hz, 3H), 6.06 (t, J = 8.4 Hz, 6H), 4.19 (s, 9H). MALDI-TOF-MS (m/z): calcd. for C<sub>78</sub>H<sub>60</sub>N<sub>9</sub>Ir: 1315.62, found: 1314.00. Anal. calcd (%) for C<sub>78</sub>H<sub>60</sub>N<sub>9</sub>Ir: C, 71.21; H, 4.60; N, 9.58. Found: C, 71.18; H, 4.64; N, 9.56.

#### **Dendrimer G2**

This compound was prepared according to the procedure for the synthesis of **G0**, with a yield of 28%. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): 7.58 (d, J = 8.0 Hz, 3H), 7.46 (d, J = 8.5 Hz, 3H), 7.14–7.08 (m, 27H), 6.92 (t, J = 7.5 Hz, 15H), 6.84 (d, J = 8.0 Hz, 21H), 6.70 (d, J = 8.5 Hz, 15H), 6.63 (br, 15H), 6.30 (d, J = 8.5 Hz, 3H), 6.22 (d, J = 8.0 Hz, 3H), 3.95 (s, 9H). MALDI-TOF-MS (m/z): calcd for C<sub>150</sub>H<sub>114</sub>N<sub>15</sub>Ir: 2318.88, found: 2317.21. Anal. calcd (%) for C<sub>150</sub>H<sub>114</sub>N<sub>15</sub>Ir: C, 77.69; H, 4.95; N, 9.06. Found: C, 77.51; H, 4.81; N, 9.14.

#### Dendrimer G2Cz

This compound was prepared according to the procedure for the synthesis of **G0**, with a yield of 27%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 8.13 (m, 12H), 7.74 (d, J = 9.0 Hz, 3H), 7.63 (d, J = 8.4 Hz, 3H), 7.37 (d, J = 8.7 Hz, 12H), 7.22–7.09 (m, 54H), 6.75 (t, J = 7.5 Hz, 3H), 6.68 (d, J = 8.7 Hz, 3H), 6.21 (d, J = 8.1 Hz, 3H), 4.09 (s, 9H). MALDI-TOF-MS (m/z): calcd. for C<sub>150</sub>H<sub>102</sub>N<sub>15</sub>Ir: 2306.79, found: 2305.79. Anal. calcd (%) for C<sub>150</sub>H<sub>102</sub>N<sub>15</sub>Ir: C, 78.10; H, 4.46; N, 9.11. Found: C, 77.87; H, 4.30; N, 9.03.

### **Results and discussion**

#### Molecular design and synthesis

Herein, we chose a phenyl benzimidazole ligand homoleptic Ir(III) complex as the chromophore, and diphenylamine-based dendrons as encapsulating groups in order to separate the phosphorescent centers. Methyl iodide was reacted with the N–H group of benzimidazole, which not only avoids interference during the following coordination process, but is also convenient to characterize the complexes by <sup>1</sup>H-NMR spectra. Moreover, there is no need to additionally introduce flexible surface groups owing to the good solubility of the branches. Considering the importance of the balance of charge transport

in a single-layer device, 2-phenylbenzimidazole is *para*substituted on the phenyl segment by the dendrons, so as to utilize the hole-transporting properties of diphenylamine groups and the electron-transporting properties of benzimidazole.

The benzimidazole (BI) derivatives were synthesized by the condensation of benzaldehyde derivatives and o-phenylenediamine in the presence of a mild catalyst, sodium metabisulfite or ammonium chloride. Then the ligands were conveniently prepared by methylation of the BI derivatives (Scheme 1). The Ir(III) complexes were prepared according to the following wellestablished, two-step approach60 (Scheme 2): the chloridebridged dimers were first formed by treating IrCl<sub>3</sub>·3H<sub>2</sub>O with excessive ligands in a mixed solvent of 2-ethoxyethanol and water. Then the crude dimers reacted with excessive ligands to convert to the facial (fac) isomer at 190 °C in glycerol. The complexes were purified through column chromatography. Notably, higher yields of G1, G2, and G2Cz compared to G0 were obtained under similar conditions due to better solubility. Therefore, the gram-scale preparation of these dendrimers became much easier. The structures of the complexes were verified using <sup>1</sup>H-NMR, MALDI-TOF-MS, and elemental analysis.

#### Thermal and phase properties

The decomposition temperatures of the complexes were determined from the thermogravimetric analysis (TGA) curves under a nitrogen atmosphere. As shown in Fig. 1, the iridium complexes were very stable under a N2 atmosphere and no significant weight loss was seen below 350 °C. The temperatures of decomposition ( $T_d$ : corresponding to 5% weight loss) of G0 and G1 are 456 °C and 436 °C, while the  $T_d$  values of G2 and G2Cz increase to 571 °C and 609 °C, respectively. It was found that the decomposition of G0 started at 360 °C, and at 610 °C the weight loss ratio was 25%, which corresponds to the loss of one ligand (M = 207) in **GO**. It means that one of the ligands in the complex decomposed with the corresponding coordination bond breaking in the temperature range mentioned above. However, the corresponding temperature ranges of G1, G2, and G2Cz, with the same weight loss of 207, are 351-678 °C, 386-771 °C, and 397-782 °C, respectively. It indicates that the rupture of the coordination bond can be retarded in the second generation dendrimers, which is obviously related to their increased molecular sizes.

In order to elucidate the phase status of the complexes in the solid, X-ray diffraction (XRD) analyses of **G0–G2Cz** were performed. As shown in Fig. 2, the four strongest sharp peaks with  $2\theta$  angles at 8°, 9°, 12°, and 21° proved the existence of crystallization in **G0**, and the size of the crystal evaluated by the Scherrer equation ( $D = 0.89 \lambda/\beta \cos \theta$ ) is 61 nm. The crystallization of **G1** was observed by the sharp peaks at 7°, 8°, and 9° which also exist in **G0**. The size of the crystal is about 81 nm. Since crystallization is the process of three-dimensional regular packing of molecules, and strong intermolecular interactions are always present to hold the molecules in the correct positions in the crystals, it indicates that the



LG2 LG2Cz:









Scheme 2 (a) Synthesis of the dendrimers with G1 as an example. (b) Molecular structures of the dendrimers G0, G1, G2 and G2Cz.



Fig. 1 TGA curves of the complexes recorded under a nitrogen atmosphere.



first-generation dendron is not large enough to completely avoid the aggregation of the Ir(m) cores. In contrast, only broad and weak peaks were found in the XRD spectra of G2 and G2Cz. Both of them are amorphous. It is clear that the highly branched structures of the molecules can remarkably decrease the crystallization tendency and stabilize the amorphous glass state of the materials. In addition, the weak intermolecular interaction and aggregation of G2 and G2Cz might have strong effects on the reduction of concentration quenching and T–T annihilation, which are necessary for high-performance PhOLEDs.

#### Photophysical properties

UV/vis and PL spectra of the ligands and the corresponding complexes were measured in their dilute  $CH_2Cl_2$  solutions (Fig. 3). The absorption peak at 292 nm of **LGO** is attributed to the benzimidazole moieties, and the other peak at 228 nm

corresponds to the phenyl moiety. For LG1, LG2, and LG2Cz, apart from the absorption peaks originating from phenyl benzimidazole, the peaks at 341 nm and 346 nm are attributed to the triphenylamine moieties and those at 261 nm and 330 nm correspond to carbazole moieties. The notable red-shift (169 nm) in the PL spectra from LG0 to LG2 could be attributed



Fig. 3 (a) The absorption and PL spectra of the ligands in  $CH_2Cl_2$  solution. (b) The absorption and PL spectra of the complexes in  $CH_2Cl_2$  solution. (c) The PL spectra of G2 in dilute  $CH_2Cl_2$  solution, neat film, and  $CH_2Cl_2$  glass.

to the increased delocalization caused by a great number of diphenylamine substitutions.

Compared with the absorption spectra of the ligands, in the absorption spectra of the complexes, the strong absorption bands below 360 nm closely resemble those of the free ligands. These short-wavelength absorptions are assigned to spinallowed ligand-centered  $\pi$ - $\pi$ \* transitions. The weak absorption shoulders in the range 360-500 nm are attributed to the metalto-ligand charge-transfer (MLCT) transitions. As seen in Fig. 3(b), the complexes in dichloromethane exhibit emission spectra with a similar shape and a red-shift of about 15 nm from G0 to G2, which is a smaller red-shift range compared with that of the ligands from LG0 to LG2 (169 nm). It indicates that as the molecular size of the complexes increases from G0 to G2 and G2Cz, the dendritic substitutions are highly twisted to the emissive center as a result of the enhanced steric hindrance effect, which limits the extent of conjugation between the central core and the branches. This means that connecting the diphenylamine dendrons to the core G0 at the para-position of the phenyl does not obviously change the optical properties, and therefore the dendrons mainly act as an encapsulation layer to separate the emissive cores from each other. The predominant ligand-centered  ${}^{3}\pi - \pi^{*}$  ( ${}^{3}LC \pi - \pi^{*}$ ) character, other than the <sup>3</sup>MLCT character of the emissive excited states, is confirmed by the vibronically structured emission spectra.<sup>61,62</sup> Furthermore, the emissions of these complexes in spin-coated films show smaller red-shifts than those in solution, which also shows their weak self-aggregation in the solid. At 77 K in CH<sub>2</sub>Cl<sub>2</sub> glass, the complexes all show more structured emission spectra, which exhibit small blue-shifts (2-3 nm) with respect to their emission spectra at room temperature, further confirming the predominant <sup>3</sup>LC  $\pi$ - $\pi$ \* character of the emissive excited states.63-65 The hypsochromic shifts are due to solvent reorganization in a fluid solution, which are significantly impeded in a rigid matrix at 77 K. Fig. 3(c) shows the PL spectra of G2 in dilute CH<sub>2</sub>Cl<sub>2</sub> solution, neat film, and CH<sub>2</sub>Cl<sub>2</sub> glass as an example.

Both the solution and film PL quantum yield  $(\Phi_p)$  of the dendrimers were measured and the data are listed in Table 1. The dendrimer G2 exhibits a neat film  $\Phi_{\rm p}$  of 28%, which is almost identical to that of G2Cz, 7 times of that of G0, and 3 times that of G1, indicative of a significantly reduced interaction between emissive Ir(m) cores with increasing generation of the dendrimers. The solution  $\Phi_{\rm p}$  of G1 (52%) is slightly higher than that of G0 (49%), but for G2 the  $\Phi_{\rm p}$  decreases to 43%, which shows a different trend compared to that in film. Interestingly, the solution  $\Phi_{\rm p}$  of G2Cz increases to 60% after introducing the carbazole end-capped diphenylamine (CzDPA) dendron to G0. The large difference between the  $\Phi_{\rm p}$  of G2 and G2Cz in organic solvent may be a result of their difference in rotational freedom.<sup>59</sup> The rotational freedom of G2Cz is lower than that of G2, for the molecular rigidity is enhanced with a substitution of carbazole end-capped units for diphenylamine units, which helps to reduce non-radiative decay processes. The rotational freedom of both G2Cz and G2 are reduced rapidly in the film, and their film  $\Phi_{\rm p}$  values are very close to each other.

The lifetimes  $(\tau)$  of these complexes were measured in degassed DMSO solution at room temperature, and their

radiative decay rates  $(K_r)$  and non-radiative decay rates  $(K_{nr})$  were calculated and listed in Table 1. For complexes **G0**, **G1** and **G2Cz**, the  $K_{nr}$  decreases as the molecular rigidity increases. The deviation from this trend for **G2** is presumably ascribed to the rotational oscillation of the peripheral diphenylamine substituents in solutions, resulting in an additional ultrafast decay process.

#### **Electrochemical properties**

To demonstrate the contribution of the diphenylamine-based dendrons to the carrier injection in the complexes, cyclic voltammetry (CV) analysis was performed (Fig. 4). The highest occupied molecular orbital (HOMO) energy levels of the dendrimers were determined from the onset of the oxidation potentials according to the equation reported by de Leeuw et al.,<sup>66</sup>  $E_{\text{HOMO}} = -(E_{\text{oxy}}^{\text{onset} \rightarrow \text{SCE}} + 4.4)$  eV, and the lowest unoccupied molecular orbital (LUMO) levels were deduced from the HOMO energy levels and energy gaps determined by the onset of absorption (Table 1). Upon the anodic sweep, G0, G1, G2, and G2Cz exhibit one, two, three and two reversible oxidation processes, respectively. No reduction signal was detected for any of the dendrimers during the cathodic scan. The relatively low oxidation potentials  $(E_{onset})$  of the complexes are ascribed to the mixture of the oxidation of Ir d orbitals and ligands. The HOMO energy levels determined from  $E_{\text{onset}}$  for G1 (-5.01 eV) and G2 (-5.00 eV) are notably higher than that of G0 (-5.15 eV). These data show that incorporation of the diphenylamine-based dendrons in G1 and G2 has a great impact on the electrochemical process and can improve their hole-injection (HI) properties. By contrast, the HOMO energy level of G2Cz decreases to -5.25 eV, which is lower than that of G2 by 0.25 eV, reflecting the fact that the outer carbazole units are electronwithdrawing through an inductive or  $\pi$ -polarization effect.

Compared with the prototype G0, dendrimers G1, G2, and G2Cz exhibit extra oxidation waves at a higher potential. The second set of reversible oxidation for G1 begins at 0.89 V, which is reasonably attributed to the oxidation of the diphenylamine units, and is consistent with the results reported by Lee et al.67 For G2, extra oxidation waves at 0.75 V and 1.02 V are observed, which are respectively attributed to the oxidation of the inner diphenylamine units as well as the outer ones. The inner ones are reversible, with the onset lower than that of G1 by 0.14 V, implying that the inner layer of G2 is more electron-rich due to the presence of  $\pi$ -donating outer diphenylamine substituents. On the other hand, G2Cz exhibits two oxidation waves besides the first reversible oxidation peak: one irreversible peak (0.97 V) corresponds to the oxidation of the inner diphenylamineunits, while the other reversible peak (1.22 V) is relevant to the oxidation of the outer carbazole dendrons. However, the onset potential of the former peak is higher than that of G1 by 0.08 V, supporting the assumption that the outer carbazole dendrons are electron-withdrawing, as elaborated in earlier sections. Therefore, both G2 and G2Cz possess oxidation potential gradients such that the outer layer is electron-poor and the inner layer is electron-rich. It is believed that the intramolecular potential gaps facilitate the intramolecular charge transfer.68

Table 1 The photophysical, electrochemical, and thermal data of the complexes

Complex $\lambda_{abs}{}^{a}$ [nm] (log $\varepsilon$ )		$\lambda_{\rm em} \left[ {\rm nm}  ight]  \Phi_{\rm p}$		$\tau^{b}  [\mu \mathrm{s}]  K_{\mathrm{r}}  (\times 10^{5})  K_{\mathrm{nr}}  (\times 10^{5})  \lambda_{\mathrm{em}}{}^{d}  [\mathrm{nm}] / T_{1}  [\mathrm{eV}]  \mathrm{HOMO/LUMO}^{e}  [\mathrm{eV}]  T_{\mathrm{d}}  [^{\circ}\mathrm{C}]$					
G0	227(4.7), 242(4.7), 298(4.6), 312(4.6),	508 <sup>a</sup> /	0.49 <sup>b</sup> /	0.64	7.7	8.0	506/2.45	-5.15/-2.74	456
G1	372(4.1), 410(3.8), 455(3.5), 483(3.1) 233(4.8), 317(4.7), 359(4.8), 397(4.7),	512 <sup>c</sup> 517 <sup>a</sup> /	$0.04^c$ $0.52^b/$	0.81	6.4	5.9	514/2.41	-5.01/-2.64	436
G2	450(4.0), 500(2.7) 229(5.0), 307(5.0), 357(5.0), 409(4.8),	$526^{c}$ $523^{a}/$	$0.09^{c}$ $0.43^{b}/$	0.93	4.6	6.2	522/2.38	-5.00/-2.64	571
6267	455(4.2), 506(2.6) 235(5.5), 294(5.1), 343(5.1), 399(4.8)	$527^{c}$	$0.28^{c}$	0.01	6.6	4.4	513/2 42	-5 25/-2 88	609
0202	453(4.0), 501(2.8)	$526^{c}$	$0.00^{\circ}$	0.91	0.0	4.4	515/2.42	-5.25/-2.88	009

<sup>*a*</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution (1 × 10<sup>-6</sup> M).  $\varepsilon$  denotes the molar extinction coefficients. <sup>*b*</sup> In degassed DMSO solutions. The  $\Phi_p$  was measured *versus* (ppy)<sub>2</sub>Ir(acac) ( $\Phi_p = 0.34$  in 2-methyltetrahydrofuran).  $\tau = 1/(K_r + K_{nr})$  and  $\Phi_p = K_r/(K_r + K_{nr})$ . <sup>*c*</sup> Neat film data measured at 298 K. <sup>*d*</sup> In CH<sub>2</sub>Cl<sub>2</sub> glass at 77 K. <sup>*e*</sup> The HOMO and LUMO energies were determined from cyclic voltammetry and absorption data.

G2Cz G2 Current / µA G1 Current SCE G0 Ag 0.2 0.4 0.6 0.8 1.0 0.0 Voltage(V) 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 Voltage(V)

**Fig. 4** CV curves of the complexes (*versus* a silver wire pseudoreference electrode). Inset: CV curves of ferrocene measured using SCE or Ag as a reference electrode.

Thus, more oxidation states might be anticipated to make the two second-generation dendrimers superior to **G1** and **G0** in hole injection and transporting.

#### Theoretical calculation

Density functional theory (DFT) calculations have also been performed to characterize the three-dimensional geometries and the frontier molecular orbitals of the complexes by employing the Gaussian 03 package (Fig. S1, ESI†). The diphenylamine-based dendrons are significantly twisted against the 2-phenylbenzimidazole (PBI), resulting from the steric hindrance effect caused by introducing the dendrons into the *para*-site of the phenyl segment of the ligands. These geometrical characteristics can effectively prevent intermolecular interactions between emitting cores, thus, suppress molecular recrystallization and limit the extent of conjugation between the central core and branches, which improves the morphological stability of the thin film and maintains the optical properties as the size of the molecule increases. Furthermore, the benzimidazole moieties concentrate on one side of the octahedral structure and the dendrons point in the opposite direction. Consequently, a flower bouquet-shaped structure is formed in the dendrimer.

The electron density contours of the three lowest unoccupied (LUMO to LUMO + 2) and the three highest occupied molecular orbitals (HOMO to HOMO + 2) for G0–G2Cz are presented. Notably, the outer diphenylamine and carbazole dendrons in G2 and G2Cz participate in the formation of the HOMOs, while the LUMOs are located on the surface of the molecules, which may lead to the increased hole and electron mobility when they act as the self-host materials. The balanced charge injection/ transporting capacities and the weak intermolecular interactions are essential for developing highly efficient non-doped phosphors suitable for low-cost single-layer device technologies.

#### **Electroluminescent properties**

Inspired by the amorphous states and excellent PL and electrochemical properties of G2 and G2Cz, the host-free devices A and B with the configuration of ITO/PEDOT:PSS/neat dendrimer/Cs<sub>2</sub>CO<sub>3</sub>/Al have been fabricated by spin-coating, where PEDOT:PSS was used as the hole-injection layer and Cs<sub>2</sub>CO<sub>3</sub> was used as the electron-injection layer. The single-layer devices A and B were based on G2 and G2Cz respectively. Fig. 5 presents the current density-voltage-luminance (J-V-L) characteristics and curves of luminance efficiency versus current density of the devices, and the main device data are collected in Table 2. The turn-on voltage of device A (4.0 V) is lower than that of B (4.3 V)due to the reduced energy barrier between the anode and emission layer of the former (Fig. 6). The HOMO and LUMO levels of G2 were embedded between the HOMO of PEDOT:PSS (-5.20 eV) and the work function of Cs<sub>2</sub>CO<sub>3</sub>/Al (-2.20 eV). Thus, it behaved as an effective trapping site for holes and electrons, which were easily injected from the two electrodes and combined in the iridium phosphor. The device A achieves a maximum current efficiency ( $\eta_{c,max}$ ) of 14.02 cd A<sup>-1</sup> and a maximum external quantum efficiency ( $\eta_{ext,max}$ ) of 4.67% photons per electron at the brightness of 147.94 cd m<sup>-2</sup>; even at a high brightness of 1000 cd m<sup>-2</sup> or 10 000 cd m<sup>-2</sup>,  $\eta_c$  is still as



Fig. 5 (a) J-V-L characteristics and (b) luminance efficiency versus current density plots and (c) EL spectra for the devices from G2 and G2Cz.



Fig. 6 Schematic energy-level diagram of the devices A and B.

high as 12.86 cd  $A^{-1}$  or 8.04 cd  $A^{-1}$ . The small values of efficiency roll-off should be attributed to the sufficiently depressed concentration quenching of the emissive core and the good charge-transporting ability of the branching units. In contrast, a similar device fabricated from **G2Cz** shows a better performance; it exhibits higher performances with  $\eta_{c,max}$  of 18.35 cd  $A^{-1}$ ,  $\eta_{ext,max}$  of 6.12%, and smaller values of efficiency roll-off than device A because of the increased hole-injection barrier and reduced electron-injection barrier to eliminate exciton quenching at the cathode interface.

We note that the EL efficiencies enabled by G2 and G2Cz are the highest ever reported for single-layer self-host green emissive devices fabricated by spin-coating (which is observed in Ding's bipolar dendrimers with  $\eta_{c,max}$  of 5.5 cd A<sup>-1</sup>,  $\eta_{ext,max}$  of 1.6%).49 The high performances indicate an efficient and balanced charge injection, transport, and combination besides the sufficiently depressed concentration quenching and T-T annihilation. With the aim of achieving a large size molecular phosphor used in host-free spin-coated devices, highly sterically hindered dendrons such as triphenylamine-based and carbazole-based dendrons are widely used. However, the performance of the single-layer device is very poor relative to that of the multilayer device, which may result from the excellent holetransporting properties, but poor electron-injection and electron-transport capabilities of these dendrons.38 The high performance of our single-layer device without introducing any additional electron-transport dendrons is profound. The dendrons were introduced at the para-position of the phenyl instead of the N-position in phenyl benzimidazole.41,42,49 This not only reduces the intermolecular interaction efficiently due to steric effects, but it also positions benzimidazole moieties on the surface rather than being trapped in the center of the molecule. Fig. 7 shows the difference between the molecular structures as well as single-layer self-host device performances of G2Cz and G2 (Ding et al.).38 It also presents the different

Table 2	Device performances of the electrophosphorescent OLEDs										
	$V_{\mathrm{on}}{}^{a}\left[\mathrm{V}\right]$	$\eta_{\mathrm{c,max}}^{b}  [\mathrm{cd}  \mathrm{A}^{-1}]$	$\eta_{\mathrm{ext,max}}^{c}$ [%]	$\eta_{\rm c}{}^d \left[{\rm cd}\;{\rm A}^{-1} ight]$	$\eta_{\mathrm{ext}}{}^{d}$ [%]	$\lambda_{\rm em}^{e} [{\rm nm}]$	$\operatorname{CIE}^{e}(x,y)$				
G2	4.0	14.02	4.67	12.86, 8.04	4.29, 2.68	526	0.37, 0.58				
G2Cz	4.3	18.35	6.12	16.52, 13.11	5.51. 4.37	524	0.38, 0.58				

<sup>*a*</sup> Recorded at 1 cd m<sup>-2</sup>. <sup>*b*</sup> Maximum current efficiency. <sup>*c*</sup> Maximum external quantum efficiency. <sup>*d*</sup> Data were measured at 1000 cd m<sup>-2</sup> and 10 000 cd m<sup>-2</sup> respectively. <sup>*e*</sup> Data were measured at 8 V.

#### Paper

three-dimensional structures caused by the substitution in different positions. The former is flower bouquet-shaped, while the latter is shaped like a ball cactus. Since the electron clouds of the LUMO levels of dendrimers were largely located on the benzimidazole moieties, the electron injection/transporting in devices A and B were improved greatly. In addition, although the electron-deficient moieties (oxadizole dendrons) have been adopted in literature,<sup>49,50</sup> the performance is still very poor due to the less efficacious electron-transport as the distance from the outer electron-deficient dendrons to the emissive core increases. Therefore, this indicates that the current molecular design is very promising for the development of solutionprocessable, single-layer self-host devices through simpler molecular structures.

## Conclusions

In this work, we have designed and synthesized a new series of homoleptic iridium(III) complexes **G0**, **G1**, **G2**, and **G2Cz** for green phosphorescent organic light-emitting devices. Our investigation showed that the introduction of diphenylaminebased dendrons is a feasible approach to realize high-efficiency small molecule phosphorescent materials in which the excellent solubility and high steric hindrance are utilized to approach solution-processing for self-host low-cost large-area

commercial applications. The second generation dendrimers G2 and G2Cz have improved thermal stability compared with the first generation dendrimer G1. XRD analysis proved that the diphenylamine-based dendrons have a strong effect on reducing the aggregation. Both G2 and G2Cz are amorphous, and they all exhibit much better PL properties in film than G0 and G1. Furthermore, the greater number of oxidation states of G2 and G2Cz might be anticipated to make it superior to G1 and G0 in hole injection and transporting. By the exposure of electron-deficient moieties on the surface of the dendrimers for balancing electron and hole fluxes, G2 and G2Cz show the best performances recorded so far for single-layer selfhost green PhOLEDs. Importantly, these materials should provide a promising strategy to develop highly efficient nondoped phosphors suitable for low-coat single-layer device technologies.

## Acknowledgements

We are grateful for grants from the National Basic Research Program China (2013CB932902), National Natural Science Foundation of China (21173042, 51103023), and the Science and Technology Support Program (Industry) Project of Jiangsu Province (BE 2013118). We also thank the support of the Key Laboratory of Novel Thin Film Solar Cells (KF201112) and the



Fig. 7 The comparison of the molecular structure as well as single-layer self-host device performance between G2Cz and G2 (Ding *et al.*).<sup>38</sup> The phenyl benzimidazole moleties of the complexes are highlighted with red circles.

State Key Laboratory of Silicon Materials Visiting Scholar Fund (SKL2011-17).

### References

- M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, 395, 151.
- 2 M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 1999, **75**, 4.
- 3 A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino and K. Ueno, *J. Am. Chem. Soc.*, 2003, 125, 12971.
- 4 R. J. Holmes, S. R. Forrest, Y. J. Tung, R. C. Kwong, J. J. Brown, S. Garon and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **82**, 2422.
- 5 W. Jiang, L. A. Duan, J. A. Qiao, G. F. Dong, D. Q. Zhang, L. D. Wang and Y. Qiu, *J. Mater. Chem.*, 2011, 21, 4918.
- 6 W. Jiang, L. Duan, J. Qiao, G. F. Dong, D. Q. Zhang,
   L. D. Wang and Y. Qiu, *Dyes Pigm.*, 2012, 92, 891.
- 7 W. Jiang, L. A. Duan, J. Qiao, D. Q. Zhang, G. F. Dong,
   L. D. Wang and Y. Qiu, *J. Mater. Chem.*, 2010, 20, 6131.
- 8 W. Jiang, Z. J. Ge, P. Y. Cai, B. Huang, Y. Q. Dai, Y. M. Sun, J. Qiao, L. D. Wang, L. Duan and Y. Qiu, *J. Mater. Chem.*, 2012, 22, 12016.
- 9 W. Jiang, J. N. Tang, W. Yang, X. X. Ban, B. Huang, Y. Q. Dai,
  Y. M. Sun, L. Duan, J. Qiao, L. D. Wang and Y. Qiu, *Tetrahedron*, 2012, 68, 5800.
- 10 W. Jiang, W. Yang, X. X. Ban, B. Huang, Y. Q. Dai, Y. M. Sun, L. Duan and Y. Qiu, *Tetrahedron*, 2012, 68, 9672.
- 11 W. Jiang, L. Duan, J. Qiao, G. F. Dong, L. D. Wang and Y. Qiu, *Org. Lett.*, 2011, **13**, 3146.
- 12 C. A. Zuniga, S. Barlow and S. R. Marder, *Chem. Mater.*, 2011, 23, 658.
- 13 E. Ahmed, T. Earmme and S. A. Jenekhe, *Adv. Funct. Mater.*, 2011, **21**, 3889.
- 14 J. S. Chen, C. S. Shi, Q. Fu, F. C. Zhao, Y. Hu, Y. L. Feng and D. G. Ma, *J. Mater. Chem.*, 2012, 22, 5164.
- 15 S. J. Hu, M. R. Zhu, Q. H. Zou, H. B. Wu, C. L. Yang, W. Y. Wong, W. Yang, J. B. Peng and Y. Cao, *Appl. Phys. Lett.*, 2012, **100**, 63304.
- 16 H. B. Wu, L. Ying, W. Yang and Y. Cao, *Chem. Soc. Rev.*, 2009, 38, 3391.
- 17 M. Cai, T. Xiao, E. Hellerich, Y. Chen, R. Shinar and J. Shinar, *Adv. Mater.*, 2011, 23, 3590.
- 18 S. L. Gong, C. L. Yang and J. G. Qin, *Chem. Soc. Rev.*, 2012, **41**, 4797.
- 19 X. H. Ouyang, D. C. Chen, S. M. Zeng, X. Y. Zhang, S. J. Su and Z. Y. Ge, *J. Mater. Chem.*, 2012, **22**, 23005.
- 20 J. Dai, K. F. Zhou, M. Li, H. Q. Sun, Y. Q. Chen, S. J. Su, X. M. Pu, Y. Huang and Z. Y. Lu, *Dalton Trans.*, 2013, 42, 10559.
- 21 H. B. Wu, G. J. Zhou, J. H. Zou, C. L. Ho, W. Y. Wong,
  W. Yang, J. B. Peng and Y. Cao, *Adv. Mater.*, 2009, 21, 4181.
- 22 B. Chen, Y. H. Li, Y. Y. Chu, A. M. Zheng, J. W. Feng, Z. T. Liu, H. B. Wu and W. Yang, *Org. Electron.*, 2013, **14**, 744.

- 23 C. Fan, Y. H. Li, C. L. Yang, H. B. Wu, J. G. Qin and Y. Cao, *Chem. Mater.*, 2012, **24**, 4581.
- 24 H. A. Al-Attar, G. C. Griffiths, T. N. Moore, M. Tavasli, M. A. Fox, M. R. Bryce and A. P. Monkman, *Adv. Funct. Mater.*, 2011, 21, 2376.
- 25 X. Q. Wei, J. B. Peng, J. B. Cheng, M. G. Xie, Z. Y. Lu, C. Li and Y. Cao, *Adv. Funct. Mater.*, 2007, **17**, 3319.
- 26 B. X. Mi, P. F. Wang, Z. Q. Gao, C. S. Lee, S. T. Lee, H. L. Hong, X. M. Chen, M. S. Wong, P. F. Xia, K. W. Cheah, C. H. Chen and W. Huang, *Adv. Mater.*, 2009, 21, 339.
- 27 L. X. Xiao, S. J. Su, Y. Agata, H. L. Lan and J. Kido, *Adv. Mater.*, 2009, **21**, 1271.
- 28 X. W. Chen, J. L. Liao, Y. M. Liang, M. O. Ahmed, H. E. Tseng and S. A. Chen, *J. Am. Chem. Soc.*, 2003, **125**, 636.
- 29 A. J. Sandee, C. K. Williams, N. R. Evans, J. E. Davies, C. E. Boothby, A. Kohler, R. H. Friend and A. B. Holmes, *J. Am. Chem. Soc.*, 2004, **126**, 7041.
- 30 H. Y. Zhen, J. Luo, W. Yang, Q. L. Chen, L. Ying, J. H. Zou,
  H. B. Wu and Y. Cao, *J. Mater. Chem.*, 2007, 17, 2824.
- 31 H. Y. Zhen, C. Y. Jiang, W. Yang, J. X. Jiang, F. Huang and Y. Cao, *Chem.-Eur. J.*, 2005, **11**, 5007.
- 32 M. Halim, J. N. G. Pillow, I. D. W. Samuel and P. L. Burn, *Adv. Mater.*, 1999, **11**, 371.
- 33 P. L. Burn, S. C. Lo and I. D. W. Samuel, *Adv. Mater.*, 2007, 19, 1675.
- 34 S. C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, O. V. Salata and I. D. W. Samuel, *Adv. Mater.*, 2002, 14, 975.
- 35 T. D. Anthopoulos, M. J. Frampton, E. B. Namdas, P. L. Burn and I. D. W. Samuel, *Adv. Mater.*, 2004, **16**, 557.
- 36 J. M. Lupton, I. D. W. Samuel, R. Beavington, M. J. Frampton,
  P. L. Burn and H. Bassler, *Phys. Rev. B: Condens. Matter*, 2001,
  63, 155206.
- 37 J. P. J. Markham, I. D. W. Samuel, S. C. Lo, P. L. Burn, M. Weiter and H. Bassler, *J. Appl. Phys.*, 2004, 95, 438.
- 38 J. Q. Ding, J. Gao, Y. X. Cheng, Z. Y. Xie, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, *Adv. Funct. Mater.*, 2006, 16, 575.
- 39 J. Q. Ding, J. Gao, Q. Fu, Y. X. Cheng, D. G. Ma and L. X. Wang, Synth. Met., 2005, 155, 539.
- 40 H. Xu, D. H. Yu, L. L. Liu, P. F. Yan, L. W. Jia, G. M. Li and Z. Y. Yue, *J. Phys. Chem. B*, 2010, **114**, 141.
- 41 L. C. Chen, Z. H. Ma, J. Q. Ding, L. X. Wang, X. B. Jing and F. S. Wang, *Org. Electron.*, 2012, **13**, 2160.
- 42 L. C. Chen, Z. H. Ma, J. Q. Ding, L. X. Wang, X. B. Jing and F. S. Wang, *Chem. Commun.*, 2011, 47, 9519.
- 43 J. Q. Ding, B. Wang, Z. Y. Yue, B. Yao, Z. Y. Xie, Y. X. Cheng, L. X. Wang, X. B. Jing and F. S. Wang, *Angew. Chem., Int. Ed.*, 2009, 48, 6664.
- 44 J. Q. Ding, J. H. Lu, Y. X. Cheng, Z. Y. Xie, L. X. Wang,
  X. B. Jing and F. S. Wang, *Adv. Funct. Mater.*, 2008, 18, 2754.
- 45 G. J. Zhou, W. Y. Wong, B. Yao, Z. Y. Xie and L. X. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1149.
- 46 M. R. Zhu, J. H. Zou, X. He, C. L. Yang, H. B. Wu, C. Zhong, J. G. Qin and Y. Cao, *Chem. Mater.*, 2012, 24, 174.

- 47 J. Q. Ding, J. H. Lu, Y. X. Cheng, Z. Y. Xie, L. X. Wang, X. B. Jing and F. S. Wang, *J. Organomet. Chem.*, 2009, 694, 2700.
- 48 W. He, D. J. Zu, D. M. Liu and R. Cheng, *Inorg. Chim. Acta*, 2011, **365**, 78.
- 49 L. C. Chen, J. Q. Ding, Y. X. Cheng, Z. Y. Xie, L. X. Wang, X. B. Jing and F. S. Wang, *Chem.-Asian J.*, 2011, 6, 1372.
- 50 J. X. Cai, T. L. Ye, X. F. Fan, C. M. Han, H. Xu, L. L. Wang, D. G. Ma, Y. Lin and P. F. Yan, *J. Mater. Chem.*, 2011, 21, 15405.
- 51 B. Liang, S. J. Hu, Y. P. Liu, Z. Q. Fan, X. Y. Wang, W. G. Zhu, H. B. Wu and Y. Cao, *Dyes Pigm.*, 2013, **99**, 41.
- 52 Y. T. Tao, Q. A. Wang, C. L. Yang, J. G. Qin and D. G. Ma, *ACS Appl. Mater. Interfaces*, 2010, 2, 2813.
- 53 M. Ichikawa, K. Hibino, N. Yokoyama, T. Miki, T. Koyama and Y. Taniguchi, *Synth. Met.*, 2006, **156**, 1383.
- 54 Q. B. Mei, L. X. Wang, Y. H. Guo, J. E. N. Weng, F. Yan, B. Tian and B. H. Tong, *J. Mater. Chem.*, 2012, 22, 6878.
- 55 X. L. Yang, Y. B. Zhao, X. W. Zhang, R. Li, J. S. Dang, Y. Li, G. J. Zhou, Z. X. Wu, D. G. Ma, W. Y. Wong, X. Zhao, A. Ren, L. X. Wang and X. Hou, *J. Mater. Chem.*, 2012, 22, 7136.
- 56 L. He, L. Duan, J. Qiao, R. J. Wang, P. Wei, L. D. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2008, **18**, 2123.

- 57 G. G. Shan, H. B. Li, Z. C. Mu, D. X. Zhu, Z. M. Su and Y. Liao, J. Organomet. Chem., 2012, 702, 27.
- 58 D. McLeod and J. McNulty, Eur. J. Org. Chem., 2012, 107, 6127.
- 59 Z. J. Ning, Z. Chen, Q. Zhang, Y. L. Yan, S. X. Qian, Y. Cao and H. Tian, *Adv. Funct. Mater.*, 2007, **17**, 3799.
- 60 A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky,
  I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.*, 2003, **125**, 7377.
- 61 M. G. Colombo and H. U. Gudel, *Inorg. Chem.*, 1993, 32, 3081.
- 62 M. S. Lowry, W. R. Hudson, R. A. Pascal and S. Bernhard, J. Am. Chem. Soc., 2004, 126, 14129.
- 63 A. B. Tamayo, S. Garon, T. Sajoto, P. I. Djurovich, I. M. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, 44, 8723.
- 64 S. Sprouse, K. A. King, P. J. Spellane and R. J. Watts, *J. Am. Chem. Soc.*, 1984, **106**, 6647.
- 65 M. G. Colombo, T. C. Brunold, T. Riedener, H. U. Gudel, M. Fortsch and H. B. Burgi, *Inorg. Chem.*, 1994, 33, 545.
- 66 D. M. deLeeuw, M. M. J. Simenon, A. R. Brown and R. E. F. Einerhand, *Synth. Met.*, 1997, 87, 53.
- 67 C. C. Lee, M. K. Leung, P. Y. Lee, T. L. Chiu, J. H. Lee, C. Liu and P. T. Chou, *Macromolecules*, 2012, **45**, 751.
- 68 M. J. Plater and T. Jackson, Tetrahedron, 2003, 59, 4673.