### Dyes and Pigments 88 (2011) 333-343



Contents lists available at ScienceDirect

# Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

# Light-emitting dyes derived from bifunctional chromophores of diarylamine and oxadiazole: Synthesis, crystal structure, photophysics and electroluminescence

Ze He<sup>a</sup>, Chi-Wai Kan<sup>b,\*,2</sup>, Cheuk-Lam Ho<sup>a</sup>, Wai-Yeung Wong<sup>a,\*,1</sup>, Chung-Hin Chui<sup>b,c,\*,3</sup>, Ka-Lap Tong<sup>d</sup>, Shu-Kong So<sup>d</sup>, Tik-Ho Lee<sup>a</sup>, Louis M. Leung<sup>a</sup>, Zhenyang Lin<sup>e</sup>

<sup>a</sup> Department of Chemistry and Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Waterloo Road, Hong Kong, P.R. China

<sup>b</sup> Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, P.R. China

<sup>c</sup> Department of Medicine and Therapeutics, Li Ka Shing Medical Sciences Building, Prince of Wales Hospital, The Chinese University of Hong Kong, Hong Kong, P.R. China

<sup>d</sup> Department of Physics, Hong Kong Baptist University, Waterloo Road, Hong Kong, P.R. China

<sup>e</sup> Department of Chemistry, The Hong Kong University of Science and Technology, Clearwater Bay, Hong Kong, P.R. China

# ARTICLE INFO

Article history: Received 19 May 2010 Received in revised form 2 August 2010 Accepted 2 August 2010 Available online 10 August 2010

Keywords: Arylamine Bipolar molecules Crystal structures Electroluminescence Organic synthesis Oxadiazole

#### 1. Introduction

# ABSTRACT

The synthesis, structural, photophysical, electrochemical and electroluminescent properties of a novel class of bifunctional molecule are reported in which the hole-transporting triarylamine and electrontransporting oxadiazole components were combined. The strongly luminescent compounds displayed good thermal and morphological stability as well as intense fluorescence both in solution and thin film at room temperature. The effects of the introduction of substituents with different electronic properties upon their absorption and emissive characteristics were correlated with theoretical calculations using density functional theory computations. The photophysics and electrochemistry of such systems were compared to those for the corresponding molecule without an oxadiazole ring. The bipolar compounds could be vacuum-sublimed and applied as emissive dopants for the fabrication of electrofluorescent, organic light-emitting devices with relatively simpler device structures, which can emit tunable colors by varying the aryl ring substituents.

© 2010 Elsevier Ltd. All rights reserved.

The launch of commercial electronic appliances incorporating organic light-emitting diodes (OLEDs) as lighting and display units has illustrated a wide range of applications for these technologies. OLEDs have the potential to replace both of these areas in the near future, offering many attractive properties and prospects [1-4]. However, there is certainly room for improvement in order for OLEDs to compete with other low-cost technologies. Certain issues including thermal stability, color purity and manufacturing yield are critical. From the production point of view, reducing the number of active layers allows a better control of the uniformity of the device and minimizing interfacial diffusion, which are the main causes for degradation and poor long-term stability in OLED operation [5]. Recently, bipolar hosts have aroused considerable

interest in OLEDs because they can balance the charge recombination which is essential for highly efficient devices [6–9]. This strategy may also negate the possibility of phase segregation and simplify the device fabrication process relative to those with multilayer structures [10–13]. However, ways need to be found to relieve the dilemma between the bipolar transporting properties and the bandgap of the material, since the electron-donating and electron-accepting units integrated on bipolar molecules inevitably lower their bandgaps by intramolecular charge-transfer [9]. Therefore, we are interested in the design and synthesis of some bipolar dyad materials that also serve as the light-emitter. These materials are typically composed of a hole-transporting (HT) block and an electron-transporting (ET) unit which can combine properties of both functional components to produce new properties that are hardly possible with either component alone [14,15]. Oxadiazole derivatives are commonly used as ET materials due to their good thermal and chemical stability as well as their high photoluminescence (PL) quantum yields, making them ideal for incorporation into OLED devices [16–19]. They usually exhibit wide bandgap properties because oxadiazole restricts extension of  $\pi$ -conjugation beyond the ring even if the molecule is coplanar [20,21]. Some bipyridyl oxadiazoles have been reported to serve as

<sup>\*</sup> Corresponding authors.

E-mail addresses: tccwk@inet.polyu.edu.hk (C.-W. Kan), rwywong@hkbu.edu.hk (W.-Y. Wong), chchui@graduate.hku.hk (C.-H. Chui).

<sup>&</sup>lt;sup>1</sup> Tel.: +852 3411 7074; fax: +852 3411 7348.

<sup>&</sup>lt;sup>2</sup> Tel.: +852 2766 6531; fax: +852 2773 1432.

<sup>&</sup>lt;sup>3</sup> Tel.: +852 2632 3120; fax: +852 2637 5396.

<sup>0143-7208/\$ –</sup> see front matter  $\odot$  2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2010.08.001

efficient and durable ET and hole-blocking molecular materials [19]. On the other hand, most HT materials are based on triarylamines since they are a well-known electron donor moiety that can promote the transport of holes [22,23]. In this article, we present the synthesis, optical properties and electroluminescent behavior of a series of new bifunctional pyridyl-based materials containing oxadiazole and triphenylamine units. Adding different substituents on the aryl ring of triphenylamine is also shown to be able to tune the emission wavelength easily.

# 2. Experimental

# 2.1. General comments

All reactions were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during work-up. Solvents were predried and distilled from appropriate drying agents. All chemicals, unless otherwise stated, were obtained from commercial sources and used as received. Preparative TLC was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF<sub>254</sub>) prepared in our laboratory. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured in appropriate solvents on a JEOL EX270 or a Varian INOVA 400 MHz FT-NMR spectrometer, with the chemical shifts quoted relative to SiMe<sub>4</sub>. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 mass spectrometer. Electronic absorption spectra were obtained with a Hewlett Packard 8453 UV-visible spectrometer. The solution emission spectra and lifetimes were measured on a Photon Technology International (PTI) Fluorescence Master Series QM1 spectrophotometer using an xenon lamp and a N<sub>2</sub> laser as the excitation source, respectively. The fluorescence quantum yields ( $\Phi$ ) were determined in CH<sub>2</sub>Cl<sub>2</sub> solutions at 298 K against the anthracene standard ( $\Phi = 0.27$ ) [24]. Thermal analyses were performed with the Perkin-Elmer TGA6 thermal analyzer at a heating rate of 20 °C min<sup>-1</sup>. Electrochemical measurements were made using a BAS CV-50 W model potentiostat. A conventional three-electrode configuration consisting of a platinum working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode was used. The solvent in all measurements was CH<sub>2</sub>Cl<sub>2</sub>, and the supporting electrolyte was 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub>. Ferrocene was added as a calibrant after each set of measurements, and all potentials reported were quoted with reference to the ferroceneferrocenium (Fc/Fc<sup>+</sup>) couple at a scan rate of 100 mV s<sup>-1</sup>. Theoretical calculations based on density functional theory (DFT) approach at the B3LYP level were performed with the use of Gaussian 03 program [25]. Experimental structures obtained from X-ray data, whenever available, were used in the calculations. The basis set used for C, N, O and H atoms was 6-31G [26]. All the MO plots were made with the use of Molden 3.5 [27]. Compound 2e was prepared according to the literature method [28,29].

# 2.2. General procedures for the preparation of 2a to 2d

These compounds were obtained using a procedure similar to that described below; in each case, a typical example is given for the fluoro derivative. 4-Tetrazolyltriphenylamine was prepared according to the literature method [10].

#### 2.2.1. Di(4-fluorophenyl)phenylamine

A mixture of 4-iodofluorobenzene (5 mL, 9.63 g, 43.36 mmol), aniline (1.83 mL, 20.00 mmol), 1,10-phenanthroline (0.75 g, 4.16 mmol), Cul (0.40 g, 4.04 mmol), KOH (10.0 g, 0.18 mmol) and xylene (50 mL) was stirred at 140 °C for 72 h. After cooling to room temperature, the mixture was added to water (200 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL  $\times$  3),

washed with water (50 mL × 3), dried over anhydrous MgSO<sub>4</sub> and the solvent removed by rotary evaporation. The product was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:10, v/v) as eluent to afford the title compound in 31% yield (1.72 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.24–7.18 (m, 2H, Ar), 7.05–6.91 ppm (m, 11H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 160.41, 156.81, 147.85, 143.80, 143.77, 129.16, 125.83, 125.72, 122.70, 122.20, 116.17, 115.83 ppm (Ar); FAB-MS: *m*/*z* 281 (M<sup>+</sup>); Anal. Calcd for C<sub>18</sub>H<sub>13</sub>NF<sub>2</sub>: C, 76.86; H, 4.66; N, 4.98. Found: C, 76.55; H, 4.43; N, 4.67.

# 2.2.2. Di(4-tolyl)phenylamine

Yellow viscous liquid from 4-iodotoluene and aniline. Yield: 53% (Eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.21–7.15 (m, 2H, Ar), 7.05–6.88 (m, 11H, Ar), 2.29 ppm (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 148.11, 145.31, 132.14, 129.70, 128.89, 124.33, 122.84, 121.59 (Ar), 20.87 ppm (CH<sub>3</sub>); FAB-MS: *m*/*z* 273 (M<sup>+</sup>); Anal. Calcd for C<sub>20</sub>H<sub>19</sub>N: C, 87.87; H, 7.01; N, 5.12. Found: C, 87.67; H, 6.88; N, 5.01.

#### 2.2.3. Di(4-methoxyphenyl)phenylamine

Yellow liquid from 1-iodo-4-methoxybenzene and aniline. Yield: 67% (Eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.25–6.79 (m, 13H, Ar), 3.79 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 155.52, 148.62, 141.04, 128.80, 126.28, 120.83, 120.47, 114.55 (Ar), 55.51 ppm (OCH<sub>3</sub>); FAB-MS: *m/z* 305 (M<sup>+</sup>); Anal. Calcd for C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub>: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.45; H, 6.04; N, 4.33.

#### 2.2.4. N,N-Di(4-fluorophenyl)aminobenzaldehyde

To a mixture of di(4-fluorophenyl)phenylamine (1.72 g, 6.12 mmol) and DMF (20 mL) at 0 °C, POCl<sub>3</sub> (1.03 g, 0.62 mL, 6.73 mmol) was added dropwise with stirring. The resulting mixture was stirred at 120 °C for 48 h and, after cooling to room temperature, was poured into ice-water (50 mL), and neutralized using 4 M aq NaOH solution (50 mL). The mixture was extracted with  $CH_2Cl_2$  (50 mL  $\times$  3), washed with water (50 mL  $\times$  3), dried over anhydrous MgSO<sub>4</sub> and the solvent removed by rotary evaporation. The residue was purified by column chromatography using hexane/ethyl acetate (3:1, v/v) as eluent to afford the target product as a yellow solid in 73% yield (1.38 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 9.77$  (s, 1H, CHO), 7.68-7.65 (m, 2H, Ar), 7.18-7.16 (m, 4H, Ar), 7.07-7.01 (m, 4H, Ar), 6.94–6.91 ppm (d, 2H, Ar);  ${}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta$  = 189.97 (CHO), 161.65, 158.03, 153.02, 141.76, 141.71, 131.20, 128.83, 127.91, 127.79, 118.16, 116.74, 116.41 ppm (Ar); FAB-MS: *m*/*z* 309 (M<sup>+</sup>); Anal. Calcd for C<sub>19</sub>H<sub>13</sub>NF<sub>2</sub>O: C, 73.78; H, 4.24; N, 4.53. Found: C, 73.67; H, 4.02; N, 4.25.

# 2.2.5. N,N-Di(4-tolyl)aminobenzaldehyde

Yellow solid from di(4-tolyl)phenylamine. Yield: 64% (Eluent: CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 9.71 (s, 1H, CHO), 7.61–7.58 (d, <sup>3</sup>J (H,H) = 8.1 Hz, 2H, Ar), 7.11–7.01 (m, 8H, Ar), 6.94–6.91 (d, <sup>3</sup>J (H,H) = 8.1 Hz, 2H, Ar), 2.30 ppm (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 189.60 (CHO), 153.17, 143.10, 134.55, 130.91, 130.01, 128.08, 126.00, 117.88 (Ar), 20.79 ppm (CH<sub>3</sub>). FAB-MS: *m/z* 301 (M<sup>+</sup>); Anal. Calcd for C<sub>21</sub>H<sub>19</sub>NO: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.40; H, 6.21; N, 4.55.

#### 2.2.6. N,N-Bis(4-methoxyphenyl)aminobenzaldehyde

Yellow solid from di(4-methoxyphenyl)phenylamine. Yield: 76% (Eluent: hexane/ethyl acetate (3:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 9.74 (s, 1H, CHO), 7.63–7.60 (m, 2H, Ar), 7.14–7.10 (m, 4H, Ar), 6.90–6.82 (m, 6H, Ar), 3.80 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 190.01 (CHO), 157.10, 153.86, 138.63, 131.26, 127.90, 127.59, 116.60, 114.93 (Ar), 55.46 ppm (OCH<sub>3</sub>); FAB-MS: *m*/*z* 333 (M<sup>+</sup>); Anal. Calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>3</sub>: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.43; H, 5.44; N, 4.10.

# 2.2.7. 4-Cyanophenyl-di(4-fluorophenyl)amine

A mixture of *N*,*N*-di(4-fluorophenyl)aminobenzaldehyde (1.38 g, 4.46 mmol), hydroxylamine hydrochloride (0.60 g, 8.63 mmol), acetic acid (1.2 mL), DMF (8 mL) and pyridine (1 mL) was added to a reaction flask and the mixture was heated to 130 °C and stirred for 9 h. After cooling to room temperature, the resulting mixture was added to CH<sub>2</sub>Cl<sub>2</sub> (50 mL), washed with water (20 mL × 3), dried over anhydrous MgSO<sub>4</sub> and the solvent removed under vacuum. The residue was purified by column chromatography eluting with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane (1:1, v/v) to give a yellow solid of the title compound (0.84 g, 61%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.43–7.39 (m, 2H, Ar), 7.16–7.01 (m, 8H, Ar), 6.89–6.86 ppm (m, 2H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 161.69, 158.08, 151.34, 141.56, 141.51, 133.10, 127.85, 127.72, 119.38, 118.48, 116.83, 116.49 (Ar), 102.32 ppm (CN); FAB-MS: *m*/*z* 306 (M<sup>+</sup>); Anal. Calcd for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>F<sub>2</sub>: C, 74.50; H, 3.95; N, 9.15. Found: C, 74.34; H, 3.77; N, 9.20.

#### 2.2.8. 4-Cyanophenyl-di(4-tolyl)amine

Yellow solid from *N*,*N*-di(4-tolyl)aminobenzaldehyde. Yield: 74% (Eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane (2:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.38–7.33 (m, 2H, Ar), 7.14–7.11 (m, 4H, Ar), 7.05–7.01 (m, 4H, Ar), 6.90–6.85 (m, 2H, Ar), 2.33 ppm (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 151.65, 143.10, 134.86, 132.90, 130.23, 126.08, 119.78, 118.39 (Ar), 101.28 (CN), 20.97 ppm (CH<sub>3</sub>); FAB-MS: *m*/*z* 298 (M<sup>+</sup>); Anal. Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.40; H, 6.16; N, 9.10.

#### 2.2.9. 4-Cyanophenyl-di(4-methoxyphenyl)amine

Yellow solid from *N*,*N*-di(4-methoxyphenyl)aminobenzaldehyde. Yield: 76% (Eluent: Hexane/ethyl acetate (3:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 9.74 (s, 1H, CHO), 7.63–7.60 (m, 2H, Ar), 7.14–7.10 (m, 4H, Ar), 6.90–6.82 (m, 6H, Ar), 3.80 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 190.01 (CHO), 157.10, 153.86, 138.63, 131.26, 127.90, 127.59, 116.60, 114.93 (Ar), 55.46 ppm (OCH<sub>3</sub>); FAB-MS: *m*/*z* 330 (M<sup>+</sup>); Anal. Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.40; H, 5.30; N, 8.34.

#### 2.2.10. 4-Tetrazolylphenyl-di(4-fluorophenyl)amine

A mixture of 4-cyanophenyl-di(4-fluorophenyl)amine (0.84 g, 2.73 mmol), NaN<sub>3</sub> (0.36 g, 5.51 mmol) and NH<sub>4</sub>Cl (0.30 g,

Table 1	1
---------	---

#### X-ray crystal data for selected molecules.

5.51 mmol) was stirred in DMF (10 mL) and the mixture was heated under reflux for 90 h. Upon cooling to room temperature, the mixture was slowly added to 2 M HCl (100 mL). The precipitate was collected and washed with water. Recrystallization from toluene gave a pale yellow solid of 4-tetrazolylphenyl-di(4-fluorophenyl) amine (0.76 g, 80%). <sup>1</sup>H NMR (*d*<sub>6</sub>-acetone):  $\delta$  = 7.97–7.93 (m, 2H, Ar), 7.25–7.12 (m, 8H, Ar), 7.02–6.99 (m, 2H, Ar), 3.23 ppm (s, 1H, NH); <sup>13</sup>C NMR (*d*<sub>6</sub>-acetone):  $\delta$  = 205.96, 162.10, 158.53, 151.22, 143.60, 143.56, 128.90, 128.50, 128.38, 120.74, 117.33, 117.00 ppm (Ar); FAB-MS: *m/z* 349 (M<sup>+</sup>); Anal. Calcd for C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>F<sub>2</sub>: C, 65.33; H, 3.75; N, 20.05. Found: C, 65.10; H, 3.80; N, 19.88.

#### 2.2.11. 4-Tetrazolylphenyl-di(4-tolyl)amine

Yellow solid from 4-cyanophenyl-di(4-tolyl)amine. Yield: 94%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.92–7.89 (m, 2H, Ar), 7.20–7.17 (m, 4H, Ar), 7.07–6.98 (m, 6H, Ar), 2.91 (s, 1H, NH), 2.32 ppm (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 144.86, 134.86, 131.12, 130.92, 130.79, 128.72, 127.19, 126.52, 120.49 (Ar), 20.86 ppm (CH<sub>3</sub>); FAB-MS: *m/z* 341 (M<sup>+</sup>); Anal. Calcd for C<sub>21</sub>H<sub>19</sub>N<sub>5</sub>: C, 73.88; H, 5.61; N, 20.51. Found: C, 73.56; H, 5.59; N, 20.32.

# 2.2.12. 4-Tetrazolylphenyl-di(4-methoxyphenyl)amine

Greenish-yellow powder from 4-cyanophenyl-di(4-methox-yphenyl)amine. Yield: 24%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.81–7.77 (m, 2H, Ar), 7.07–7.03 (m, 4H, Ar), 6.89–6.80 (m, 6H, Ar), 3.76 (s, 6H, OCH<sub>3</sub>), 2.97 ppm (s, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 156.66, 149.91, 139.28, 128.17, 127.51, 118.32, 116.38, 114.89, 114.64 (Ar), 55.53 ppm (OCH<sub>3</sub>); FAB-MS: *m/z* 373 (M<sup>+</sup>); Anal. Calcd for C<sub>21</sub>H<sub>19</sub>N<sub>5</sub>O<sub>2</sub>: C, 67.55; H, 5.13; N, 18.75. Found: C, 67.30; H, 5.22; N, 18.55.

#### 2.2.13. Compound 1a

A mixture of 4-tetrazolylphenyl-di(4-fluorophenyl)amine (0.76 g, 2.18 mmol), 4-bromobenzoyl chloride (0.60 g, 2.73 mmol) and dry pyridine (8 mL) was stirred and heated under reflux for 48 h. After being cooled to room temperature, the mixture was added to CH<sub>2</sub>Cl<sub>2</sub> (100 mL), washed with water (30 mL  $\times$  3), dried over anhydrous MgSO<sub>4</sub> and the solvent was stripped off under reduced pressure. The residue was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent to afford a yellow solid of **1a** (0.77 g, 70%). <sup>1</sup>H

Compound	1c	1d	2a	2b	2c	2e
formula	C <sub>28</sub> H <sub>22</sub> N <sub>3</sub> BrO·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>28</sub> H <sub>22</sub> N <sub>3</sub> BrO <sub>3</sub>	C31H20N4F2O	C <sub>31</sub> H <sub>22</sub> N <sub>4</sub> O	C <sub>31</sub> H <sub>22</sub> N <sub>4</sub> O	C <sub>23</sub> H <sub>18</sub> N <sub>2</sub>
formula weight	581.32	528.40	502.51	466.53	494.58	322.39
crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
space group	P21/c	$P2_1/c$	Ρī	Ρī	$P2_1/c$	$P2_{1}2_{1}2_{1}$
a (Å)	14.144 (2)	14.1179 (6)	9.3204 (7)	10.768 (1)	13.5476 (9)	10.1593 (8)
b (Å)	10.145 (1)	17.8171 (7)	11.9915 (9)	11.761 (2)	11.5633 (8)	12.752 (1)
<i>c</i> (Å)	18.584 (3)	9.5858 (4)	12.1553 (9)	19.961 (3)	17.222 (1)	13.275 (1)
$\alpha$ (deg)	90	90	73.676 (1)	103.368 (2)	90	90
$\beta$ (deg)	95.938(2)	90.358(1)	83.694 (1)	98.022 (2)	98.903 (1)	90
$\gamma$ (deg)	90	90	77.613 (1)	101.334 (3)	90	90
$V(Å^3)$	2652.3 (7)	2411.2(2)	1271.7 (2)	3836 (2)	2665.3 (3)	1719.9 (2)
Ζ	4	4	2	4	4	4
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.456	1.456	1.312	1.310	1.233	1.245
$\mu (\mathrm{mm}^{-1})$	1.779	1.741	0.092	0.081	0.076	0.073
F(000)	1184	1080	520	976	1040	680
$\theta$ range (deg)	2.20-25.00	1.84-25.00	1.80-28.25	1.86-25.00	2.13-25.00	2.52 - 25.00
reflections collected	10619	11799	7611	11831	12915	8591
unique reflections	4218	4238	5523	8164	4667	3022
R <sub>int</sub>	0.1139	0.0221	0.0142	0.0236	0.0171	0.0162
observed reflections	2164	3303	3078	4509	3719	2750
no. of parameters	325	298	343	244	343	226
R1, wR2 $[I > 2.0\sigma(I)]^{a}$	0.0428, 0.0917	0.0304, 0.0561	0.0480, 0.1292	0.0456, 0.1110	0.0521, 0.1542	0.0294, 0.0728
R1, wR2 (all data)	0.1224, 0.1158	0.0592, 0.0647	0.0932, 0.1586	0.1035, 0.1376	0.0643, 0.1708	0.0341, 0.0766
GoF on F <sup>2b</sup>	0.857	1.039	0.996	0.955	1.030	1.024

<sup>a</sup> R1 =  $\sum ||F_0| - |F_c|| / \Sigma |F_0|$ . wR2 = { $\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]$ }<sup>1/2</sup>.

<sup>b</sup> GoF =  $[(\sum w|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$ .

NMR (CDCl<sub>3</sub>):  $\delta$  = 7.99–7.90 (m, 4H, Ar), 7.68–7.64 (m, 2H, Ar), 7.16–6.98 ppm (m, 10H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 164.53, 163.14, 161.42, 157.82, 150.93, 142.32, 142.27, 132.27, 128.07, 127.44, 127.32, 126.03, 122.91, 119.73, 116.72, 116.39, 115.51 ppm (Ar); FAB-MS: *m/z* 504 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>16</sub>N<sub>3</sub>BrF<sub>2</sub>O: C, 61.92; H, 3.20; N, 8.33. Found: C, 61.78; H, 3.10; N, 8.43.

# 2.2.14. Compound 1b

Pale yellow powder from 4-tetrazolyltriphenylamine. Yield: 62% (Eluent: CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.00–7.97 (m, 2H, Ar), 7.94–7.91 (m, 2H, Ar), 7.68–7.65 (m, 2H, Ar), 7.36–7.31 (m, 4H, Ar), 7.19–7.09 ppm (m, 8H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 164.77, 163.23, 151.04, 146.53, 132.34, 129.59, 128.14, 128.02, 126.06, 125.71, 124.45, 123.00, 120.92, 115.64 ppm (Ar); FAB-MS: *m/z* 468 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>18</sub>N<sub>3</sub>BrO: C, 66.68; H, 3.87; N, 8.97. Found: C, 66.65; H, 3.56; N, 8.77.

# 2.2.15. Compound 1c

Yellow powder from 4-tetrazolylphenyl-di(4-tolyl)amine. Yield: 80% (Eluent: CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.98–7.95 (m, 2H, Ar), 7.89–7.86 (m, 2H, Ar), 7.66–7.62 (m, 2H, Ar), 7.14–7.01 (m, 10H, Ar),

2.34 ppm (s, 6H, CH<sub>3</sub>);  ${}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta$  = 164.72, 162.92, 151.21, 143.80, 134.18, 132.18, 130.11, 128.00, 127.83, 125.85, 125.77, 122.99, 119.59, 114.60 (Ar), 20.99 ppm (CH<sub>3</sub>); FAB-MS: *m/z* 496 (M<sup>+</sup>); Anal. Calcd for C<sub>28</sub>H<sub>22</sub>N<sub>3</sub>BrO: C, 67.75; H, 4.47; N, 8.46. Found: C, 67.49; H, 4.32; N, 8.50.

# 2.2.16. Compound 1d

Yellow solid from 4-tetrazolylphenyl-di(4-methoxyphenyl) amine. Yield 65% (Eluent: CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (10:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.97–7.93 (m, 2H, Ar), 7.87–7.83 (m, 2H, Ar), 7.65–7.61 (m, 2H, Ar), 7.14–7.09 (m, 4H, Ar), 6.94–6.86 (m, 6H, Ar), 3.81 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 164.75, 162.77, 156.68, 151.59, 139.14, 132.13, 127.94, 127.82, 127.50, 125.75, 122.98, 117.87, 114.83, 113.67 (Ar), 55.44 ppm (OCH<sub>3</sub>); FAB-MS: *m*/*z* 528 (M<sup>+</sup>); Anal. Calcd for C<sub>28</sub>H<sub>22</sub>N<sub>3</sub>BrO<sub>3</sub>: C, 63.65; H, 4.20; N, 7.95. Found: C, 63.51; H, 4.10; N, 7.84.

# 2.2.17. Compound 2a

A mixture of 2-(tri-*n*-butylstannyl)pyridine (0.53 g, 1.43 mmol), Pd (PPh<sub>3</sub>)<sub>4</sub> (0.10 g, 0.09 mmol) and **1a** (0.46 g, 0.92 mmol) was stirred in toluene (20 mL) and the mixture was heated to 110  $^{\circ}$ C for 50 h. Upon



#### Scheme 1. Synthesis of bifunctional compounds and their bromide precursors.

cooling to room temperature, the solvent was removed by rotary evaporation and the residue was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent to afford the title compound as a yellow powder (0.28 g, 61%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.74–8.72 (m, 1H, Ar), 8.23–8.15 (m, 4H, Ar), 7.97–7.93 (m, 2H, Ar), 7.82–7.80 (m, 2H, Ar), 7.32–7.27 (m, 1H, Ar), 7.16–7.11 (m, 4H, Ar), 7.07–7.00 ppm (m, 6H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 164.58, 163.81, 160.93, 158.49, 155.97, 150.93, 149.88, 142.46, 142.43, 142.11, 136.94, 128.15, 127.46, 127.42, 127.38, 127.15, 124.27, 122.84, 120.77, 119.87, 116.70, 116.48, 115.80 ppm (Ar); FAB-MS: *m/z* 503 (M<sup>+</sup>); Anal. Calcd for C<sub>31</sub>H<sub>20</sub>N<sub>4</sub>F<sub>2</sub>O: C, 74.09; H, 4.01; N, 11.15. Found: C, 73,98; H, 4.08; N, 11.02.

# 2.2.18. Compound 2b

а

Yellow powder from **1b**. Yield: 48% (CH<sub>2</sub>Cl<sub>2</sub>:ethyl acetate (5:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.75-8.72$  (m, 1H, Ar), 8.24–8.15 (m, 4H, Ar), 7.99–7.94 (m, 2H, Ar), 7.82–7.79 (m, 2H, Ar), 7.36–7.27 (m, 5H, Ar), 7.19–7.09 ppm (m, 8H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 164.54$ , 163.64, 155.87, 150.85, 149.76, 146.49, 141.98, 136.82, 129.49, 127.95, 127.34, 127.07, 125.59, 124.31, 124.26, 122.73, 120.97, 120.69, 115.88 ppm (Ar); FAB-MS: *m/z* 467 (M<sup>+</sup>); Anal. Calcd for C<sub>31</sub>H<sub>22</sub>N<sub>4</sub>O: C, 79.81; H, 4.75; N, 12.01. Found: C, 79.87; H, 4.56; N, 11.89.

#### 2.2.19. Compound 2c

Yellow solid from **1c**. Yield: 85% (CH<sub>2</sub>Cl<sub>2</sub>:ethyl acetate (5:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.70 (m, 1H, Ar), 8.20–8.11 (m, 4H, Ar), 7.91–7.88 (m, 2H, Ar), 7.77–7.73 (m, 2H, Ar), 7.26–7.21 (m, 1H, Ar), 7.13–7.01 (m, 10H, Ar), 2.33 ppm (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 164.48, 163.32, 155.62, 150.98, 149.56, 143.72, 141.70, 136.65, 133.98, 129.99, 127.72, 127.14, 126.84, 125.62, 124.14, 122.57, 120.48, 119.50, 114.72 (Ar), 20.89 ppm (CH<sub>3</sub>); FAB-MS: *m*/*z* 495 (M<sup>+</sup>); Anal. Calcd for C<sub>33</sub>H<sub>26</sub>N<sub>4</sub>O: C, 80.14; H, 5.30; N, 11.33. Found: C, 80.20; H, 5.15; N, 11.16.

# 2.2.20. Compound 2d

Yellow solid from **1d**. Yield: 67% (CH<sub>2</sub>Cl<sub>2</sub>:ethyl acetate (10:1, v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.74–8.72 (m, 1H, Ar), 8.23–8.14 (m, 4H, Ar), 7.91–7.88 (m, 2H, Ar), 7.81–7.79 (m, 2H, Ar), 7.31–7.26 (m, 1H, Ar), 7.15–7.12 (m, 4H, Ar), 6.96–6.87 (m, 6H, Ar), 3.82 ppm (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 164.76, 163.42, 156.71, 155.92, 151.58, 149.74, 141.87, 139.32, 136.79, 127.90, 127.53, 127.30, 127.01, 124.38, 122.69, 120.66, 118.06, 114.89, 114.05 (Ar), 55.52 ppm (OCH<sub>3</sub>); FAB-MS: *m*/*z* 527 (M<sup>+</sup>); Anal. Calcd for C<sub>33</sub>H<sub>26</sub>N<sub>4</sub>O<sub>3</sub>: C, 75.27; H, 4.98; N, 10.64. Found: C, 75.11; H, 5.08; N, 10.44.



b

Fig. 1. X-Ray crystal structures of (a) 1c, (b) 1d, (c) 2a, (d) 2b, (e) 2c and (f) 2e.

# Table 2

Photophysical data for **2a–2e**.

Compound	$T_{\text{decomp}}$ (°C)	$\lambda_{max}  (nm)^a$	Emission in CH <sub>2</sub> Cl <sub>2</sub> (298 K)	
			$\lambda_{\rm em}  ({\rm nm})^{\rm b}$	Φ (%) <sup>c</sup>
2a	466	293 (54.1)	462 (3.74)	81.1
		364 (66.9)		
2b	456	294 (65.6)	472 (4.15)	70.0
		368 (71.2)		
2c	466	296 (50.3)	499 (4.60)	57.0
		375 (52.3)		
2d	421	294 (21.7)	537 (2.71)	40.0
		375 (22.3)		
2e	341	347 (21.7)	429 (3.12)	89.2

<sup>a</sup> Extinction coefficients  $(10^4 \text{ M}^{-1} \text{ cm}^{-1})$  are shown in parentheses.

<sup>b</sup> Fluorescence lifetimes (ns) are shown in parentheses.

 $^{\rm c}\,$  Fluorescence quantum yields were determined against the anthracene standard ( $\Phi=0.27).$ 

# 2.3. X-ray crystallography

Single crystals suitable for X-ray crystallographic analyses were grown by slow evaporation of their respective solutions in CH<sub>2</sub>Cl<sub>2</sub>/ hexane at room temperature. Important crystal data pertinent to individual compounds and the structure refinement results are assemblied in Table 1. The diffraction experiments were carried out at 293 K on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo-K<sub>a</sub> radiation  $(\lambda = 0.71073 \text{ Å})$ . The raw intensity data frames were integrated with the SAINT+ program using a narrow-frame integration algorithm [30]. Corrections for Lorentz and polarization effects were also applied by SAINT. For each analysis, an empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS [31]. The structures were solved by the Direct Methods, and expanded by difference Fourier syntheses using the software SHELTXL [32]. Structure refinements were made on  $F^2$  by the full-matrix least-squares technique. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their ideal positions but not refined. CCDC numbers 776173-776178.

#### 2.4. OLED fabrication and measurements

Before device fabrication, the ITO coated glass substrates were ultrasonically cleaned in organic solvents followed by ozone

 Table 3
 Electrochemical properties and frontier orbital energy levels of 2a-2e.

Complex	$E_{\rm g}({\rm eV})$	$E_{1/2}^{\rm ox} (V)^{\rm a}$	HOMO (eV) <sup>b</sup>	LUMO (eV) <sup>c</sup>
2a	3.00	+0.76	-5.56	-2.56
2b	2.99	+0.66	-5.47	-2.48
2c	2.95	+0.54	-5.34	-2.39
2d	2.90	+0.37, +0.98 (i)	-5.17	-2.27
2e	3.25	+0.46	-5.26	-2.01

i = irreversible wave.

<sup>a</sup> 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>, versus ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple.

 $^{\rm b}$  HOMO level was calculated by using the ferrocene value of 4.8 eV below the vacuum level.

<sup>c</sup> Estimated from the HOMO and bandgap energies (LUMO =  $E_g$  + HOMO).

treatment. The single-layer devices were assembled in the following sequence: indium tin oxide (ITO) with sheet resistance of 80  $\Omega$  per square on glass substrate (anode), 15 nm of CuPc (hole-injection layer), 0 or 60 nm of TPD (hole-transport layer), 60 or 80 nm of the emitter, 30 nm of Ca and 80 nm of Al (cathode). The organic layers were evaporated and laminated in the above sequence under  $4 \times 10^{-6}$  Torr without breaking vacuum between each vacuum deposition process. The organic and electrode layers were deposited at a rate of 1 and 10 Å per second, respectively. The thickness of each layer was measured in situ by a quartz crystal sensor and ex situ by a stylus profilometer (Tencor  $\alpha$ -step 500). The EL spectra were measured by a Larry 2048L CCD system and current-voltage-luminance characteristics were recorded in air with a Keithley 236 source measuring unit and International Light Corporation (Model ILC1400) light meter.

#### 3. Results and discussion

#### 3.1. Synthesis

Scheme 1 shows the chemical structure and the synthetic strategies leading to the bifunctional molecules in the present study. First, the *N*-arylation of aniline was carried out by the modified Ullmann condensation with the corresponding *p*-iodoarene under the CuCl/phen/KOH catalytic system to give the substituted triarylamines [33–35]. Formylation of substituted triarylamines with POCl<sub>3</sub> in DMF affords diphenylaminobenzaldehyde which can be derivatized to 4-cyanotriphenylamine using a hydroxylamine hydrochloride/acetic acid/pyridine mixture and then to 4-tetrazolyltriphenylamine via the use of NaN<sub>3</sub>/NH<sub>4</sub>Cl. The key bipolar products **2a–2d** in this work can be obtained from



Fig. 2. Absorption spectra of 2a-2d at 298 K.



Fig. 3. PL spectra of **2a**-**2d** at 298 K.

4-tetrazolyltriphenylamine [10] by a two-step reaction. 4-Tetrazolyltriphenylamine reacts with 4-bromobenzoyl chloride to give **1a–1d** which can then undergo Stille coupling with 2-(tributylstannyl)pyridine using  $Pd(PPh_3)_4$  as the coupling catalyst to afford **2a–2d** [36]. Likewise, compound **2e** was also synthesized from (4-bromophenyl)diphenylamine for comparative purposes.

<sup>1</sup>H and <sup>13</sup>C NMR analyses clearly indicate that a well-defined structure has been obtained in each compound. In all cases, <sup>1</sup>H NMR resonances arising from the protons of the organic moieties were observed. The *ortho* proton on the pyridyl ring shows a characteristic downfield resonance ( $\delta$  8.70–8.74). The remaining aromatic protons appear in the region  $\delta$  6.8–8.2 with accurate integrals. The methyl substituents in **2c** give rise to a sharp singlet at  $\delta$  2.33, while

the methoxy protons of **2d** appear as a singlet at  $\delta$  3.82. In the <sup>13</sup>C NMR spectra, a total of 19 carbon resonances for **2b** and 20 signals for both **2c** and **2d** were observed that are consistent with their formulations. The spectroscopic data shown in the Experimental Section are in line with their assigned structures.

# 3.2. X-ray crystal structures

The three-dimensional molecular structures of **1c**, **1d**, **2a**, **2b**, **2c** and **2e** were confirmed by X-ray crystallography. Perspective drawings of compounds are shown in Fig. 1. Among **2a**–**2c**, each of them consists of a diarylaminophenyl unit covalently linked to an oxadiazole ring and a pendant free 2-pyridyl group is attached to

(-84.09 kJ mol<sup>-1</sup>) LUMO+1



(-158.03 kJ mol-1) LUMO



(-482.91 kJ mol<sup>-1</sup>) HOMO



(-595.83 kJ mol<sup>-1</sup>) HOMO-1

Fig. 4. Contour plots of the frontier molecular orbitals for 2c.

another phenyl ring. These molecules are notably twisted which can be attributed to the large space torsion disrupting the  $\pi$ -conjugation between triarylamine and oxadiazole moieties for the molecules. The oxadiazole plane makes dihedral angles of 23.8 and 10.9° (5.0 and 4.7°; 9.2 and 8.9°) with the amine-bonded and pyridyl-bonded phenyl rings, respectively, for **2a** (**2b**; **2c**).

# 3.3. Thermal and photophysical properties

The thermal properties of **2a**–**2d** were examined by thermogravimetric analysis (TGA). All of the compounds generally exhibit high thermal stability and their onset decomposition temperatures ( $T_{decomp}$ ) range from 421 to 466 °C (Table 2). Relative to **2e**, incorporation of an oxadiazole ring notably increases the thermal stability of **2a**–**2d**. In addition, they can be easily sublimed at low pressures (~ 10<sup>-6</sup> Pa) without thermal decomposition.

The absorption and emission data of **2a**–**2e** are shown in Table 2. For **2a**–**2d**, two distinct absorption bands were observed at 293–296 and 364–375 nm, which are attributed to the  $\pi$ – $\pi$ \* transitions associated with the N–Ar and N–C<sub>6</sub>H<sub>4</sub>–X fragments (Fig. 2). Similar data were observed in the spectra of Ar<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub>–X species near 300 and 350 nm [37,38]. An analogous ligand system containing a 2,2'-bipyridyl unit also shows absorption features at 316 and 388 nm [39]. While the higher energy absorption peak does not change with the R groups among **2a**–**2d**, the lower-lying band is slightly blue-shifted by electron-withdrawing units ( $\lambda_{max} = 364$  nm) and red-shifted by electron-donating moieties ( $\lambda_{max} = 375$  nm) with respect to **2b** ( $\lambda_{max} = 368$  nm). Due to the twisted molecular configuration of **2a**–**2d**, they show inhibited intramolecular charge-transfer and high bandgaps ( $E_g$ ) (see Table 3).

Each of **2a**–**2d** is a good light-emitter in both solution and solid state at 298 K. The photoluminescence (PL) spectrum of 2a-2d is dominated by intraligand  $(\pi - \pi^*)$  transitions in the visible region and the emissions vary from 462 to 537 nm (Fig. 3). Like the absorption spectra, for 2a-2d, the emissions are sensitive to the para-substituents on the Ar<sub>2</sub>N group and the emission wavelength is affected by the electronic properties of R in the order: OMe > Me > H > F. In other words, compound **2a** which contains electron-withdrawing fluoro-substituted triphenylamine shows a hypsochromic-shifted emission, while those with electronreleasing substituents (-Me 2c and -OMe 2d) undergo bathochromic-shifted emission with respect to the unsubstituted congener **2b**. This is a clear manifestation of the fact that the position occupied by the substituents in the arylamine moiety would dominate the HOMO character so that the electron-donating and -accepting groups can raise and lower the HOMO levels, respectively (vide infra).

#### 3.4. DFT calculations

Molecular orbital calculations at the B3LYP level of density functional theory (DFT) were performed on **2a–2d** to study their electronic structures. The HOMO mainly consists of an out-of-phase combination between the  $\pi$  orbitals of the three N(amine)-bonded phenyl rings and the amine–N p $_{\pi}$  orbital while the LUMO is derived from the  $\pi$  orbitals of the oxadiazole ring and the phenylpyridine group (Fig. 4). The DFT results indicate that the feature of the frontier molecular orbitals does not change significantly with different substituents. The calculated HOMO–LUMO gaps for **2a–2e** follow the order: **2d** (315.51 kJ mol<sup>-1</sup>) < **2c** (325.15 kJ mol<sup>-1</sup>) < **2b** (342.52 kJ mol<sup>-1</sup>) < **2a** (368.57 kJ mol<sup>-1</sup>) < **2e** (383.05 kJ mol<sup>-1</sup>) (1 eV = 96.485 kJ mol<sup>-1</sup>). It was shown that the Ar<sub>2</sub>N groups effectively determine the properties of HOMOs. The trend is expected because the highly electronegative –F substituent tends to stabilize the HOMO significantly, giving the largest energy gap

Table 4
---------

|--|

Device	V <sub>turn-on</sub> (V)	Luminance (cd m <sup>-2</sup> )	$\eta_{\rm L}$ (cd A <sup>-1</sup> )	$\eta_{ m p}$ (lm W <sup>-1</sup> )	λ <sub>max</sub> (nm)	CIE
A	7.2	896 (13.4 V) <sup>a</sup>	0.53 <sup>a</sup> 0.50 <sup>b</sup> 0.49 <sup>c</sup>	0.19 <sup>a</sup> 0.17 <sup>b</sup> 0.13 <sup>c</sup>	464	(0.19, 0.25)
В	8.0	364 (12.6 V) <sup>a</sup>	0.19 <sup>a</sup> 0.07 <sup>b</sup> 0.17 <sup>c</sup>	0.05 <sup>a</sup> 0.02 <sup>b</sup> 0.05 <sup>c</sup>	458	(0.18, 0.18)
С	5.4	868 (12.8 V) <sup>a</sup>	0.98 <sup>a</sup> 0.66 <sup>b</sup> 0.51 <sup>c</sup>	0.54 <sup>a</sup> 0.25 <sup>b</sup> 0.15 <sup>c</sup>	480	(0.27, 0.36)
D	5.2	728 (10.8 V) <sup>a</sup>	0.93 <sup>a</sup> 0.82 <sup>b</sup> 0.59 <sup>c</sup>	0.43 <sup>a</sup> 0.33 <sup>b</sup> 0.19 <sup>c</sup>	478	(0.26, 0.36)
Е	5.4	3864 (13.6 V) <sup>a</sup>	2.19 <sup>a</sup> 2.15 <sup>b</sup> 2.00 <sup>c</sup>	0.87 <sup>a</sup> 0.81 <sup>b</sup> 0.57 <sup>c</sup>	508	(0.25, 0.52)
F	4.8	3080 (12.4 V) <sup>a</sup>	1.63 <sup>a</sup> 1.60 <sup>b</sup> 1.37 <sup>c</sup>	0.92 <sup>a</sup> 0.68 <sup>b</sup> 0.45 <sup>c</sup>	512	(0.23, 0.51)

<sup>a</sup> Maximum values of the devices.

<sup>b</sup> At 20 mA cm<sup>-2</sup>.

<sup>c</sup> At 100 mA cm<sup>-2</sup>.

among **2a**–**2d**, while the strongly electron-donating –OMe group gives the smallest gap. The HOMO of **2e** is mainly related to an out-of-phase combination between the  $\pi$  orbitals of the three N (amine)-bonded phenyl rings and the amine–N p $_{\pi}$  orbital while the LUMOs are derived mainly from  $\pi^*$  orbitals of the pyridine ring. The gap calculated for **2e** is greater than those calculated for **2a**–**2d**, probably due to the fact that the  $\pi$  system of **2e** is less extensively delocalized.

# 3.5. Redox behavior

In order to investigate the electronic effects caused by the addition of R groups, cyclic voltammetry experiments were carried out for all compounds. Due to the limited electrochemical window available in  $CH_2Cl_2$  and the inability of our instrument to measure the reduction potentials in the range -2.7 to -3.5 V, we obtained only the oxidation potentials for our compounds and the LUMO



**Fig. 5.** The general structure for OLED devices and the molecular structures of the compounds used. CuPc: copper phthalocyanine; TPD: *N*,*N*'-diphenyl-*N*,*N*'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine; ITO: indium tin oxide.

levels were estimated from the HOMO and bandgap values (Table 3) [40]. Reversible oxidation waves in the range of 0.37–0.76 V were observed for **2a**–**2d** that can be assigned to the oxidation of the triphenylamine moiety. It is noteworthy that **2a**–**2d** reveal a gentle decrease in the oxidative potentials in the sequence F > H > Me > OMe, which is a manifestation of the electronic effect induced by the R substituents (viz. negative effect for –F and positive effect for both –Me and –OMe). As compared to **2e**, the LUMO level was obviously lowered by oxadiazole addition in **2a**–**2d**, signaling their added ET trait. Generally, the lower the LUMO level of the material, the better its electron injection property is. Such energy levels may provide a closer match to the work function of Al when it is used as the ET material in OLEDs.

#### 3.6. Organic electroluminescence

We also investigated the electroluminescent (EL) behavior of **2b**–**2d** in OLED devices and the results are summarized in Table 4.

Fig. 5 depicts the general structures for the OLED devices and the molecular structures of the compounds employed. *N*,*N*'-Diphenyl-*N*,*N*'-bis(3-methylphenyl-1,1'-biphenyl-4,4'-diamine) (TPD) acts as the HT layer and copper(II) phthalocyanine (CuPc) is a buffer layer for hole-injection. The device revealed a typical diode behavior, i.e., under the forward bias (a positive voltage that was applied to the ITO electrode), the current increased sharply with the increase of applied voltage after exceeding the turn-on voltage ( $V_{turn-on}$ ). Moreover, under reverse bias, no obvious increase of current was observed when the applied voltage was increased. Fig. 6 depicts the current density–voltage–luminance (J-V-L) curves and EL spectra of all the devices.

Devices **A**, **C** and **E** were built using **2b**, **2c** and **2d**, respectively, and the corresponding EL emission was observed at 464, 480 and 508 nm (Fig. 6), which is consistent with each of their corresponding PL spectra. In other words, the electrofluorescence energy depends on the nature of R groups and color tuning is made feasible by appropriate substitution of aryl rings. The EL efficiencies were



Fig. 6. J-V-L characteristics and EL spectra of devices (a) A and B, (b) C and D, and (c) E and F.

generally shown to be higher for the emitters with electrondonating substituents than the unsubstituted one. There is no emission from TPD in each case which implies that transport of holes through the TPD layer can occur and therefore holes can be effectively injected into the emissive layer to result in EL emission in our devices. Also, with the absence of any electron-transporting laver in these devices, we were still able to get moderate device performance. All these results clearly indicate that the active laver consisting of our compounds **2b–2d** serves as a light-emitter and an electron-transporting molecule in each case of devices A, C and **E**. Interestingly, devices **B**, **D** and **F** containing a sole active layer between the bilayer anode (ITO/CuPc) and cathode (Ca/Al) can also give good EL spectra akin to those of devices A, C and E. This implies that **2b**–**2d** are essentially good bipolar small-molecule materials with both hole- and electron-transporting features. However, similar device design with the configuration ITO/**2b**-**2d**/Alg<sub>3</sub>/Ca/Al (Alq<sub>3</sub>: tris(8-hydroxyquinolinato)aluminum) only afforded the Alq<sub>3</sub> green emission near 520 nm, suggesting that the bifunctional dye has a less effective HT characteristics than TPD. Hence, a slightly better performance was obtained for the devices with TPD than those without TPD. Work is still needed to further optimize the device performance.

#### 4. Conclusions

In conclusion, the present work reports the synthesis and characterization of some new light-emitting bifunctional organic materials incorporating both hole-transporter triarylamine and electron-transporter oxadiazole units, study of their structural and photophysical properties and their applications in simple monochromatic OLEDs. Modification of the para-substituents on the NAr<sub>2</sub> groups effectively facilitates the fine-tuning of the emission energy for the compounds and their HOMO/LUMO levels. End-capping of the molecules with a diarylamino unit has been shown to offer advantages in terms of lowering the first ionisation potential, which improves the HT properties. The presence of an electron-deficient oxadiazole ring can lower the LUMO level which endows these functional molecules with enhanced ET features. Their possible multifunctionality as bipolar organic emitters/phosphorescent hosts and ligand precursors for the generation of new phosphorescent metal complexes would render these materials promising for further investigations.

# Acknowledgements

W.-Y. W thanks the Hong Kong Research Grants Council (HKBU 202709) and the Hong Kong Baptist University (FRG2/08-09/111) for financial support. C.-W. Kan wishes to acknowledge the financial support to this work from The Hong Kong Polytechnic University (A-PD1G).

#### References

- Tang CW, VanSlyke SA, Chen CH. Electroluminescence of doped organic thin films. J Appl Phys 1989;65:3610–6.
- [2] Lu W, Mi BX, Chan MCW, Hui Z, Che CM, Zhu N, et al. Structural and spectroscopic studies on Pt…Pt and π–π interactions in luminescent multinuclear cyclometalated platinum(II) homologues tethered by oligophosphine auxiliaries. J Am Chem Soc 2004;126:4958–71.
- [3] Ma Y, Che CM, Chao HY, Zhou X, Chan WH, Shen J. High luminescence gold(I) and copper(I) complexes with a triplet excited state for use in light-emitting diodes. Adv Mater 1999;11:852–7.
- [4] O'Brien DF, Baldo MA, Thompson ME, Forrest SR. Improved energy transfer in electrophosphorescent devices. Appl Phys Lett 1999;74:442–4.
- [5] Shirota Y. Organic materials for electronic and optoelectronic devices. J Mater Chem 2000;10:1–25.
- [6] Kamtekar KT, Wang C, Bettington S, Batsanov AS, Perepichka IF, Bryce MR, et al. New electroluminescent bipolar compounds for balanced charge-

transport and tuneable colour in organic light emitting diodes: triphenylamine-oxadiazole-fluorene triad molecules. J Mater Chem 2006;16:3823-35.

- [7] Tao Y, Wang Q, Shang Y, Yang C, Liang A, Qin J, et al. Multifunctional bipolar triphenylamine/oxadiazole derivatives: highly efficient blue fluorescence, red phosphorescence host and two-color based white OLEDs. Chem Commun; 2009:77–9.
- [8] Tao Y, Wang Q, Yang C, Wang Q, Zhang Z, Zou T, et al. A simple carbazole/ oxadiazole hybrid molecule: an excellent bipolar host for green and red phosphorescent OLEDs. Angew Chem Int Ed 2008;47:8104–7.
- [9] Tao Y, Wang Q, Ao L, Zhong C, Qin J, Yang C, et al. Molecular design of host materials based on triphenylamine/oxadiazole hybrids for excellent deep-red phosphorescent organic light-emitting diodes. J Mater Chem 2010;20:1759–65.
- [10] Tamoto N, Adachi C, Nagai K. Electroluminescence of 1,3,4-oxadiazole and triphenylamine-containing molecules as an emitter in organic multilayer light emitting diodes. Chem Mater 1997;9:1077–85.
- [11] Wong WY, He Z, So SK, Tong KL, Lin Z. A multifunctional platinum-based triplet emitter for OLED applications. Organometallics 2005;24:4079–82.
- [12] Wong WY, Ho CL. Functional metallophosphors for effective charge carrier injection/transport: new robust OLED materials with emerging applications. J Mater Chem 2009;19:4457–82.
- [13] Wong WY, Ho CL. Coord Chem Rev 2009;253:1709-58.
- [14] Lu J, Hill AR, Sun Y, Hay AS, Maindron T, Dodelet JP. Synthesis and characterization of a blue light emitting polymer containing both hole and electron transporting units. Chem Mater 1999;11:2501–7.
- [15] Bing YJ, Leung LM, Menglian G. Synthesis of efficient blue and red light emitting phenanthroline derivatives containing both hole and electron transporting properties. Tetrahedron Lett 2004;45:6361–3.
- [16] Adachi C, Tsutsui T, Saito S. Blue light-emitting organic electroluminescent devices. Appl Phys Lett 1990;56:799–801.
- [17] Brown AR, Bradley DDC, Burroughes JH, Friend RH, Greenham NC, Burn PL, et al. Poly(p-phenylenevinylene) light-emitting diodes: enhanced electroluminescent efficiency through charge carrier confinement. Appl Phys Lett 1992;61:2793–5.
- [18] He Z, Wong WY, Yu X, Kwok HS, Lin Z. Phosphorescent platinum(II) complexes derived from multifunctional chromophores: synthesis, structures, photophysics, and electroluminescence. Inorg Chem 2006;45:10922–37.
- [19] Ichikawa M, Kawaguchi T, Kobayashi K, Miki T, Furukawa K, Koyama T, et al. Bipyridyl oxadiazoles as efficient and durable electron-transporting and holeblocking molecular materials. J Mater Chem 2006;16:221–5.
- [20] Mitschke U, Bäuerle P. The electroluminescence of organic materials. J Mater Chem 2000;10:1471–507.
- [21] Strohriegl P, Grazulevicius JV. Charge-transporting molecular glasses. Adv Mater 2002;14:1439–52.
- [22] Bender TP, Graham JF, Duff JM. Effect of substitution on the electrochemical and xerographic properties of triarylamines: correlation to the Hammett parameter of the substituent and calculated HOMO energy level. Chem Mater 2001;13:4105–11.
- [23] Casalbore-Miceli G, Esposti AD, Fattori V, Marconi G, Sabatini C. A correlation between electrochemical properties and geometrical structure of some triarylamines used as hole transporting materials in organic electroluminescent devices. Phys Chem Chem Phys 2004;6:3092–6.
- [24] Dawson WR, Windsor MW. Fluorescence yields of aromatic compounds. J Phys Chem 1968;72:3251–60.
- [25] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian03, revision B05. Pittsburgh, PA: Gaussian, Inc.; 2003.
- [26] Wadt WR, Hay PJ. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem Phys 1985;82:284–98.
- [27] Schaftenaar G. Molden, version 3.5. Toernooiveld: Nijmegen, The Netherlands: CAOS/CAMM Center Nijmegen; 1999.
- [28] Zhou G, Ho CL, Wong WY, Wang Q, Ma D, Wang L, et al. Manipulating chargetransfer character with electron-withdrawing main-group moieties for the color tuning of iridium electrophosphors. Adv Funct Mater 2008;18:499–511.
- [29] Zhou G, Wang Q, Ho CL, Wong WY, Ma D, Wang L, et al. Robust tris-cyclometalated iridium(III) phosphors with ligands for effective charge carrier injection/transport: synthesis, redox, photophysical, and electrophosphorescent behavior. Chem Asian J 2008;3:1830–41.
- [30] SAINT+, version 6.02a; Bruker analytical X-ray system. Madison, WI: Inc.; 1998.
- [31] Sheldrick GM. SADABS, empirical absorption correction program. Germany: University of Göttingen; 1997.
- [32] Sheldrick GM. SHELXTL™, Reference manual, version 5.1. WI: Madison,; 1997.
- [33] Hassan J, Sévignon M, Gozzi C, Schulz E, Lemaire M. Aryl-aryl bond formation: one century after the discovery of the Ullmann reaction. Chem Rev 2002;102:1359–69.
- [34] Martínez-Palau M, Perea E, López-Calahorra F, Velasco D. Synthesis of luminescent *N*-arylcarbazoles by copper bronze-mediated reaction. Lett Org Chem 2004;1:231–7.
- [35] Moroz AA, Shvartsberg MS. The Ullmann ether condensation. Russ Chem Rev 1974;43:679–89.
- [36] Stille JK. The palladium-catalyzed cross-coupling reactions of organotin reagents with organic electrophiles. Angew Chem Int Ed 1986;25:508–24.
- [37] Low PJ, Paterson MAJ, Goeta AE, Yufit DS, Howard JAK, Cherryman JC, et al. The molecular structures and electrochemical response of "twisted" tetra(aryl) benzidenes. J Mater Chem 2004;14:2516–23.
- [38] Low PJ, Paterson MAJ, Puschmann H, Goeta AE, Howard JAK, Lambert C, et al. Crystal, molecular and electronic structure of N, N'-diphenyl-N, N'-bis

- (2,4-dimethylphenyl)-(1,1'-biphenyl)-4,4'-diamine and the corresponding radical cation. Chem Eur J 2004;10:83–91.
  [39] Gong X, Ng PK, Chan WK. Trifunctional light-emitting molecules based on rhenium and ruthenium bipyridine complexes. Adv Mater 1998;10:1337–40.
- [40] Ho CL, Wong WY, Zhou GJ, Yao B, Xie Z, Wang L. Solution-processible multi-component cyclometalated iridium phosphors for high-efficiency orange-emitting OLEDs and their potential use as white light sources. Adv Funct Mater 2007;17:2925–36.