Dyes and Pigments 96 (2013) 278–286

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

2-Phenyl-1,2,3-benzotriazole Ir(III) complexes with additional donor fragment for single-layer PhOLED devices

D. Tomkute-Luksiene [a], J. Keruckas [a], T. Malinauskas [a], J. Simokaitiene [a], V. Getautis [a,**], J.V. Grazulevicius [a,*], D. Volyniuk [b], V. Cherpak [b], P. Stakhira [b,***], V. Yashchuk [c], V. Kosach [c], G. Luka [d], J. Sidaravicius [e]

[a] Faculty of Chemical Technology, Kaunas University of Technology, 50254 Kaunas, Lithuania
[b] Lviv Polytechnic National University, 79013 Lviv, Ukraine
[c] Kyiv Taras Shevchenko National University, Faculty of Physics, 03680 Kyiv, Ukraine
[d] Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland
[e] Department of Polygraphic Machines, Vilnius Gediminas Technical University, 03224 Vilnius, Lithuania

ARTICLE INFO

Article history:
Received 28 June 2012
Received in revised form
10 August 2012
Accepted 14 August 2012
Available online 23 August 2012

Keywords:
Iridium complexes
Triphenylamines
Carbazoles
Single-layer organic light emitting diode
Vacuum deposition
Phosphorescence

ABSTRACT

Phosphorescent bis-cyclometallated iridium (III) complexes based on 2-phenyl-1,2,3-benzotriazole with additional donoric diphenylamine or carbazole moieties were synthesized, studied and tested as phosphorescent materials in the single-layer phosphorescent organic light emitting diodes. These single-layer devices were fabricated employing a simple technological approach, based upon the simultaneous vacuum deposition from one crucible of host material and the corresponding phosphorescent 1,2,3-triazole-based iridium complexes. Red and orange electrophosphorescent single-layer devices with current efficiencies of 5.3 cd/A and 6.8 cd/A respectively are reported. Results of the impedance spectroscopy suggest that the proposed method of formation of the working layer provides homogeneous distribution of molecular guest in the matrix of host.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted a great deal of interest because of their potential applications in full-color flat-panel displays and lighting sources [1]. In recent years a lot of effort has been concentrated on the development of luminescent transition-metal complexes, particularly of the second- and third-row transition metals [2]. As a result of efficient spin–orbit coupling in these complexes, both singlet and triplet excitons can be harvested, and theoretically up to 100% internal quantum efficiencies can be attained.

In order to efficiently extract the electro-generated emissive excitons in typical electrophosphorescent device (PhOLED), various functional layers for charge carrier injection, transport, blocking, as well as the confinement of exciton diffusion, are required [3]. Such sophisticated device configuration inevitably increases the manufacturing complexity and the production cost. It is therefore highly desirable to fabricate PhOLEDs with the simplified device structure. Particularly attractive goal is the single layer device, which can perform at the comparable efficiency as its multilayer counterparts. Efficient bi-layered devices consisting of emissive and buffer layers have been reported by several researchers [4–10]. However, the single-layer approach, adopting direct charge injection and transport onto the triplet dopants dispersed in an appropriate host matrix, is quite rare and only a very limited number of publications have been reported to date [11–17].

In the past few years various nitrogen-containing heterocycles such as quinolines, isoquinolines, quinazolines, and quinoxalines have been of special interest in accomplishing efficient orange and red phosphorescent emission from iridium complexes [18]. However, 1,2,3-triazoles have been overlooked and only recently few examples have been published [19–23]. The aim of the present

---

[*] Corresponding author. Tel.: +370 37 300193; fax: +370 37 456525.
[**] Corresponding author. Tel.: +370 37 300196; fax: +370 37 300152.
[***] Corresponding author. Tel.: +380 50 2006563.
E-mail addresses: vytautas.getautis@ktu.lt (V. Getautis), juozas.grazulevicius@ktu.lt (J.V. Grazulevicius), stakhira@polynet.lviv.ua (P. Stakhira).

http://dx.doi.org/10.1016/j.dyepig.2012.08.012

work was synthesis and characterization of orange and red-emitting 1,2,3-triazole-based iridium complexes bearing hole-transporting carbazolyl or diphenylamine moieties, and investigation of their suitability for the fabrication of the single-layer electrophosphorescent devices. The single-layer PhOLEDs were fabricated employing a simple technological approach, based upon the simultaneous vacuum deposition from one crucible of host material **CBM4** (Fig. 1a) and one of the phosphorescent emitting 1,2,3-triazole-based iridium complexes, red **IC1** (Fig. 1b) or orange **IC2** (Fig. 1c), at the ratio of 90% (**CBM4**): 10% (**IC1** or **IC2**).

2. Experimental details

2.1. Materials

All chemicals were purchased from Aldrich and used as received without further purification. The details of the synthesis of 5-amino-2-phenyl-1,2,3-benzotriazole are described in Ref. [24]. 1,1-Bis(4-(3′,3″-dimethoxy)triphenylamino)cyclohexane (**CBM4**) was prepared by the earlier reported procedure [25].

2.2. General

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova spectrometer (^{1}H-300 MHz, ^{13}C-75 MHz) at room temperature. The chemical shifts are expressed in ppm, downfield from tetramethylsilane (TMS), used as internal standard. The course of the reactions was monitored by TLC on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyzer. MS were recorded on an Agilent 110 (series MS with VL) apparatus. Cyclic voltammetry (CV) measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte, Ag/AgNO$_3$ as the reference electrode and a Pt wire counter electrode. Thermogravimetric analysis (TGA) was performed with a Netzch STA 409 PC Luxx at a scan rate 10 K/min under a nitrogen flow. Differential scanning calorimetry measurements were carried out on TA Instruments Q10 calorimeter at a heating rate of 10 °C/min in the nitrogen atmosphere. The glass transition temperatures (T_g) for the investigated compounds were determined during the second heating scan.

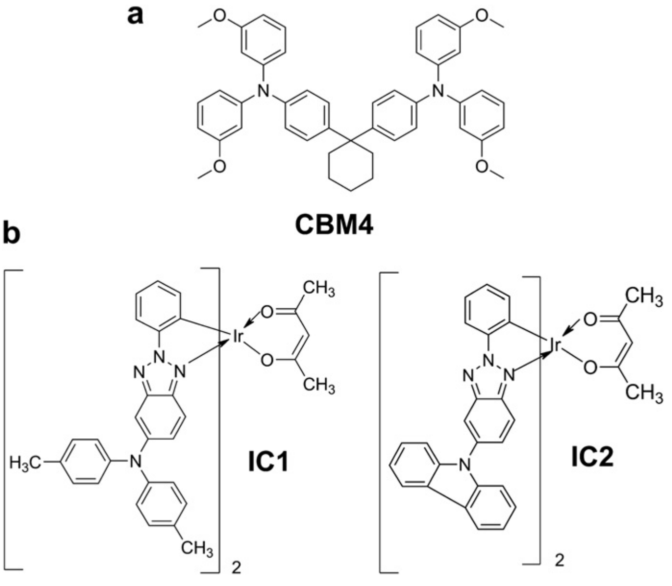

Fig. 1. Chemical structures of **CBM4**, **IC1**, **IC2**.

2.2.1. 5-Bis[(4-methylphenyl)amino]-2-phenyl-1,2,3-benzotriazole (*1*)

5-Amino-2-phenyl-1,2,3-benzotriazole (1.0 g, 4.76 mmol), 4-iodotoluene (2.59 g, 11.9 mmol), copper(I) iodide (0.033 g, 0.17 mmol), 2,2′-bipiridyl (0.027 g, 0.17 mmol) and potassium *tert* − butoxide (1.602 g, 14.28 mmol) were refluxed in 15 ml of dry toluene under argon atmosphere for 3 h. After termination of the reaction (TLC, *n*-hexane/acetone, 4:1 v/v) the mixture was filtered off and the solvent was evaporated. The residue was purified by column chromatography using *n*-hexane/acetone (24:1 v/v) as an eluent to afford **1** (0.78 g, 42%) as a yellow to orange solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ, ppm: 8.29 (dd, J = 8.7 Hz, J = 1.2 Hz, 2H), 7.73 (dd, J = 9.3 Hz, J = 0.9 Hz, 1H), 7.51 (m, 2H), 7.39 (m, 1H), 7.31 (dd, J = 2.1 Hz, J = 0.9 Hz, 1H), 7.23 (dd, J = 9.3 Hz, J = 2.1 Hz, 1H), 7.14–7.03 (m, 8H), 2.34 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ, ppm: 147.90, 146.34, 145.17, 142.03, 140.48, 133.39, 130.20, 129.49, 128.50, 126.51, 125.22, 120.18, 118.46, 106.94. MS (APCI$^+$, 20 V) *m/z*: 391 [M + H]$^+$. Anal. Found: C, 79.87; H, 5.60; N, 14.53. C$_{26}$H$_{22}$N$_4$ requires C, 79.97; H, 5.68, N, 14.35%.

2.2.2. Iridium(III)-bis{5-bis[(4-methylphenyl)amino]-2-phenyl-1,2,3-benzotriazolato-N,C2′}acetyl-acetonate (*IC1*)

Iridium trichloride hydrate (0.47 g, 1.57 mmol) and **1** (1.3 g, 3.33 mmol) were dissolved in the mixture of 2-ethoxyethanol (20 ml) and water (2.5 ml). The mixture was refluxed under argon atmosphere for 20 h, and cooled down to ambient temperature. The formed crystals were filtered and washed with water and then ethanol. The product was dried under vacuum, and used in next step without further purification. The yield of the μ-chloride-bridged dimer was 1.18 g (37%).

The μ-chloride-bridged dimer (1.18 g, 0.586 mmol), 2,4-pentanedione (0.176 g, 1.75 mmol) and sodium carbonate (0.62 g, 5.85 mmol) were refluxed in 20 ml of degassed 2-ethoxyethanol under argon atmosphere for 2 h. After termination of the reaction (TLC, *n*-hexane/acetone, 4:1 v/v) the mixture was cooled down to ambient temperature and diluted with water (10 ml). The formed solid was isolated by filtration, washed with water and ethanol. The product was purified by column chromatography using *n*-hexane/acetone (24:1 and 23:2 v/v) as the eluent to obtain **IC1** (0.94 g, 78%) as red solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ, ppm: 7.82–7.71 (m, 3H), 7.54–7.46 (m, 1H), 7.37–7.32 (m, 1H), 7.30–7.00 (m, 19H), 6.97–6.88 (m, 2H), 6.78–6.68 (m, 2H), 6.25–6.12 (m, 2H), 5.08 (s, 1H), 2.40–2.30 (m, 12H), 1.82 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ, ppm: 186.61, 186.08, 185.44, 149.58, 148.01, 145.58, 144.96, 144.90, 143.56, 142.89, 142.70, 140.63, 138.65, 134.59, 133.98, 133.73, 130.40, 130.30, 129.44, 128.14, 127.41, 125.69, 125.46, 122.43, 119.39, 115.65, 114.94, 106.54, 103.26, 103.21, 101.62, 28.36, 27.33, 27.12, 21.12; Anal. Found: C, 63.84; H, 4.55; N, 10.57. C$_{57}$H$_{49}$IrN$_8$O$_2$ requires C, 63.97; H, 4.61, N, 10.47%.

2.2.3. 2-Phenyl-5-iodo-1,2,3-benzotriazole (*2*)

Solution of 5-amino-2-phenyl-1,2,3-benzotriazole (8.4 g, 39.95 mmol) in acetic acid (150 ml) and hydrochloric acid (60 ml) was heated to 80 °C and the obtained brown suspension was then cooled down to 0 °C. Sodium nitrite (3.7 g, 53.62 mmol) in water (20 ml) was added slowly and the temperature was held at 0–5 °C throughout the addition. The resulting mixture was stirred for 45 min below 5 °C and then potassium iodide (9.6 g, 57.87 mmol) solution in water (40 ml) was added. The reaction mixture was warmed up to ambient temperature and then heated at 50 °C for 20 min. The mixture was cooled down to ambient temperature and