Organic Electronics 25 (2015) 21–30

Contents lists available at ScienceDirect

Organic Electronics

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

Solution-processed blue phosphorescent OLEDs with carbazole-based polymeric host materials

Frédéric Dumur[a,b,*], Layla Beouch[c], Sebastien Peralta[c], Guillaume Wantz[b,d], Fabrice Goubard[c], Didier Gigmes[a]

[a] Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire ICR, UMR 7273, F-13397 Marseille, France
[b] CNRS, IMS, UMR 5218, F-33400 Talence, France
[c] LPPI, Université de Cergy-Pontoise, 5 mail Gay Lussac, Neuville sur Oise, 95031 Cergy-Pontoise Cedex, France
[d] Bordeaux INP, IMS, UMR 5218, F-33400 Talence, France

ARTICLE INFO

Article history:
Received 31 March 2015
Received in revised form 28 May 2015
Accepted 5 June 2015
Available online 8 June 2015

Keywords:
FIrpic
Blue dopant
Polymer LED
Electroluminescence
Carbazole
Solution

ABSTRACT

A new carbazole-based polymer PEPEK varying from the previously reported PEPK by the length of the spacer between the polymer backbone and the pendent carbazole moiety was investigated as polymeric host for solution-processed devices. Interestingly, if the two polymers are structurally close since the length of the alkyl chain only differs from one carbon atom, the previously reported PEPK gave higher performances than the newly synthesized PEPEK when tested as host for the wide bandgap triplet emitter FIrpic. To optimize electroluminescence performances, two device configurations were examined. On doping the emissive layer of phosphorescent organic light-emitting devices (OLEDs) at 16 wt% with FIrpic, best PEPK-based OLEDs gave an efficacy of 15.14 cd/A whereas PEPEK-based devices furnished an efficiency of 12.17 cd/A in the same conditions. To determine the origin of this unexpected behavior, the new polymer PEPEK was characterized by UV–visible absorption and luminescence spectroscopy as well as cyclic voltammetry. Thermal properties of PEPEK were also examined and compared to those of PEPK.

1. Introduction

Since the first report of Burroughes et al. [1] on polymers light-emitting devices (PLEDs) utilizing a conjugated polymer as the light-emitting material, PLEDs have come a long way. Tremendous advances have been achieved [2–4], mainly through the replacement of the fluorescent emitters by phosphorescent ones [5,6]. Indeed, in these devices, both electro-generated singlet and triplet excitons contribute to light emission, enabling to reach an internal quantum efficiency of 100% [7,8]. Among all triplet emitters under investigations, iridium complexes have been identified as the most promising candidates as these organometallic complexes have high photoluminescence quantum yields at room temperature, relatively short excited state lifetimes and excellent color tunability [9]. So far, neutral [10–14], cationic [15–18], anionic [19–20] and even soft salts [21–23] where both the anionic and the cationic complex can contribute to light emission were successfully used as triplet emitters for electroluminescent devices. In phosphorescent organic light-emitting devices (OLEDs), the emitter is normally used as a guest (e.g. as a dopant) diluted into a host material in order to reduce key-adverse factors such as triplet–triplet annihilation and concentration quenching (TTA) [24–27]. In this approach, energy is transferred from both the singlet and triplet excited states of the host to the singlet and triplet excited states of the guest. It constitutes the main energy transfer mechanism. But, direct excitation of the guest by charge trapping can also occur, constituting a second electroluminescence pathway [28–29]. Accordingly, the development of both efficient emitters and host materials are of equal importance to fabricate highly emissive devices [30]. With aim at facilitating the device elaboration, solution-processable hosts are actively researched but their design is not an easy task due to the numerous requirements. Among the most important features, the charge transportation, the film-forming ability, the thermal stability, the HOMO–LUMO gap and the energy level of the triplet excited state can be cited as the main criteria to consider for designing an efficient host material [31]. Regarding PLEDs, development of blue-emitting devices is still far behind the other colors due to the lack of suitable polymeric hosts [32–34]. Up to now, poly(*N*-vinylcarbazole) (PVK) has undoubtedly been one of the most common polymeric host for

---

[*] Corresponding author at: Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire ICR, UMR 7273, F-13397 Marseille, France.

E-mail address: frederic.dumur@univ-amu.fr (F. Dumur).

http://dx.doi.org/10.1016/j.orgel.2015.06.013

wide bandgap emitters [35–37]. However, PVK clearly underperforms with blue triplet emitters [38–43]. As main figure of merit, PVK benefits from a high triplet energy level (3.0 eV) that is nearly identical to that of a single carbazole unit as a result of its non-conjugated character [44]. As main drawbacks, this unipolar polymer suffers from an imbalanced charge carrier transportation and an HOMO energy level mismatching the workfunction of common anodes [45–48]. Recently, several carbazole-based polymeric hosts that could advantageously replace PVK were reported. Notably, a polymer with a triplet energy level at 2.96 eV [49] could successfully host the well-known blue dopant iridium(III) [*bis*(4,6-difluoro-phenyl)pyridinato-*N*,C^2]picolinate FIrpic [50]. A maximum current efficiency (CE) of 23.3 cd/A could be obtained with the double-layered PLEDs. While using an iridium complex specially designed to prevent self-quenching, the best polymer (PEPK) of the series of carbazole-based polymeric hosts only differing by their polymer backbones and the length of the alkyl spacer used to attach the carbazole pendent group to the polymer chain furnished blue-emitting devices with the remarkable CE of 19.7 cd/A [51]. In the same spirit, a styrene-derived poly(carbazole) (PVAK) varying from PVK by the polymeric unit gave blue PLEDs with a CE of 18.25 cd/A while using FIrpic as the dopant [52]. Investigations on carbazole-based hosts were not limited to non-conjugated polymers and polymeric hosts with a disrupted π-conjugated main chain [53–55] or dendrimers [56,57] also furnished high performances with FIrpic or even more blue triplet emitters.

In this article, a new carbazole-based polymer (PEPEK) was studied as a host for solution-processed blue PLEDs. To evidence the interest of this new polymer, a benchmark blue triplet emitter (i.e. FIrpic) was selected as the dopant and two standard device configurations were studied. To evaluate the host ability of PEPEK, a comparison was established with PEPK, previously studied in the literature in a really specific context since a non-commercially available blue dopant was used [51]. Therefore, in this study, host ability of PEPK has been re-examined with the most classical benchmark blue dopant. Noticeably, the two polymers (PEPEK and PEPK) only differ from each other by the length of the spacer introduced between the pendant carbazole group and the polymer main chain. In devices, PEPK furnished higher performances than PEPEK whatever the device configuration, indicating the detrimental effect of the additional —CH_2— group on the electroluminescence performances.

2. Experimental section

2.1. General informations

Absorption and emission spectra were recorded with a UV MC2 spectrophotometer from the SAFAS Monaco Society and a Photon Technology International spectrofluorimeter. Absolute fluorescence quantum yields in solution and in the solid state were measured by a Hamamatsu Photonics Quantaurus QY at room temperature. Atomic force microscopy (AFM) experiments were performed in ScanAsyst mode with a Nanoscope V controller coupled at Icon microscope from Bruker.

2.2. Syntheses of the monomer and polymers

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. ^1H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^1H (400 MHz) and ^{13}C (100 MHz). The ^1H chemical shifts were referenced to the solvent peak $CDCl_3$ (7.26 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77 ppm). 9-(2-(Oxiran-2-yl)ethyl)-9*H*-carbazole (EPEK) [58] was synthesized as previously reported, without modifications and in similar yield. PEPEK was polymerized by adapting a literature procedure [51]. PEPK was prepared as previously reported [51]. Number average molecular weights, M_n, were determined by GPC using a Waters 515 HPLC gel permeation chromatography (GPC). Measurements were performed in THF solvent at room temperature with a 1 mL/min flow and calibration based on polystyrene standards. Cyclic voltammetry (CV) was performed using a multi-channel VMP potentiostat (Biologic Scientific Instrument) at a scan rate of 25 mV/s, at room temperature in THF solution (10^{-2} M), with tetrabutylammonium perchlorate at 0.1 M concentration as the supporting electrolyte. The working and the counter electrodes were a Pt disc and a Pt wire respectively, whereas Ag wire was used as a pseudo-reference electrode. Ferrocene was used as the internal standard material. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) curves were obtained respectively with a TA thermal analyzer (TA Instrument Q100 calorimeter) and a TA thermal analyzer (TA Instrument Q50) at a heating rate of 20 °C min^{-1} under argon flow. The temperature of thermal degradation (T_d) was measured at the point of 5% weight loss.

Synthesis of poly[9-(oxiran-2-yl)ethyl)-9H-carbazole] PEPEK

$BF_3.O(C_2H_5)_2$ (0.1 wt% with respect to the monomer) was added to a solution of EPEK in dry 1,2-dichloromethane so that the initial concentration of monomer was 1 mol/L. The reaction was stirred at room temperature for 20 h. The resulting polymer was isolated by precipitation in methanol containing aqueous ammonia (added for the neutralization of the initiator). Low-molecular-weight fractions were removed from the polymer by Soxhlet extraction with methanol. The polymer was obtained as a white amorphous powder in 83% yield. ^1H NMR ($CDCl_3$) δ (ppm): 0.94–1.45 (m, 2H, CH_2), 2.96–3.37 (m, 4H, CH_2O, CH_2), 3.62–4.13 (m, 2H, CH_2N), 6.53–7.63 (m, 6H), 7.98–8.25 (m, 2H); M_n = 7380 g/mol, M_w/M_n = 1.22.

2.3. PLEDs fabrication and measurements

All materials except the polymeric hosts used in the devices were purchased from Lumtec with the best purity available and used as received. PLEDs were fabricated onto cleaned indium tin oxide (ITO) glass substrates with sheet resistance of 10–12 Ω/sq. Prior to organic layer deposition, the ITO substrates were successively washed with acetone, ethanol and isopropanol under ultrasonic for 15 min before surface treatment with UV-ozone plasma for 20 min. This was followed by coating a 40 nm thick layer of poly(ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) on the treated ITO sheets at 4000 rpm for 60 s. The film was baked at 120 °C for 30 min under reduced pressure and the substrates were loaded in a glove box. A solution of host polymer (20 mg/mL in 1,2-dichlorobenzene) with *bis*(4,6-difluorophenylpyridinato)picolate iridium (III) (FIrpic) ((20 mg/mL in chloroform) was spin-coated at various spin-coating rates (3000–6000 rpm) on top of the PEDOT:PSS/ITO coated glass substrate under ambient conditions from a mixture of the two solutions. Next, evaporation of the organic layers (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), *tris*(8-quinolinolato)aluminum(III) (Alq_3) or 1,3,5-*tris*(*N*-phenyl-benzimidizol-2-yl)benzene (TPBI) was carried out under secondary vacuum. Finally, a 1-nm-thick LiF layer and an 80-nm-thick aluminum cathode layer were successively deposited on the substrates in high vacuum environment through a shadow mask. The resulting devices had the following