



Charge-transporting blue emitters having donor and acceptor moieties

D. Gudeika^a, A. Ivanauskaite^a, R. Lygaitis^a, V. Kosach^b, D. Volyniuk^a, R. Butkute^a,
A.P. Naumenko^b, V. Yashchuk^b, J.V. Grazulevicius^{a,*}^a Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254, Kaunas, Lithuania^b Kyiv Taras Shevchenko National University, Physics Faculty, UA-03680 Kiev, Ukraine

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ABSTRACT

Hole-transporting derivative of phenanthro[9,10-d]imidazole and triphenylamine and electron-transporting derivative of carbazole and 1,8-naphthalimide were synthesized and characterized. The synthesized compounds exhibited high thermal stability with the temperatures of the onsets of the thermal decomposition (463 °C and 438 °C). They showed blue emission in solutions. Relatively high hole mobility of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the layer of 2-[4-(diphenylamino)phenyl]-1-phenyl-1*H*-phenanthro[9,10-d]imidazole, and electron mobility exceeding $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the layer of 2,7-di((*N*-(2-ethylhexyl)-1,8-naphthalimide)-4-yl)-9-(2-ethylhexyl)-9*H*-carbazole were recorded by time of flight technique. The molecular mixtures consisting of the newly synthesized dyes with the commercial phosphorescent dye bis(2-phenylbenzothiazolato-*N,C*(2'))iridium(acetylacetonate) [$\text{Ir}(\text{acac})_3$] and poly[9-(2,3-epoxypropyl)carbazole] as a polymer host were prepared and studied. The colour characteristics of the photoluminescence of the obtained molecular mixtures were found to be close to those of the white light. It is suggested that in the studied molecular mixtures both Ir-based phosphorescent and fluorescent dyes can effectively absorb excitons from the polymer matrix.

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1. Introduction

White organic light-emitting devices (WOLED) attract great attention because of their potential high efficiency, good color (CRI, CIE) and contrast characteristics. They are of particular interest for lighting application where WOLED can noticeably reduce energy consumption [1,2].

In this context WOLEDs have a number of advantages over other types of the luminescent devices. The large-area flexible devices can be fabricated by convenient and relatively cheap roll-to-roll technology [3–7].

Nearly 75% of the electrically generated excitons produced in the emissive layers of OLEDs are triplet excitons [8,9]. Thus, emitter which can effectively harvest the triplet excitons is necessary for the fabrication of high-efficiency devices. For this purpose specific phosphorescent emitters were developed [10,11]. Blue phosphorescent emitters are often relatively unstable and incompatible with host matrices [12,13]. For these reasons fluorescent emitters are often used for the fabrication of blue devices.

One of the most promising variations of emissive layers of WOLED is hybrid fluorescent/phosphorescent layer on the base of

ambipolar polymer matrix in which singlet and triplet excitons are harvested by the blue fluorescent and phosphorescent emitters, respectively [14–18]. However, many blue fluorescent emitters still suffer from insufficient stability and color characteristics [17–21]. Consequently development and characterization of new stable and efficient blue fluorescent emitters for WOLED is an important task.

In this work we report on the synthesis, thermal, electrochemical and photoelectrical properties of new blue fluorescent dyes. The molecular mixtures of the newly synthesized dyes with red phosphor molecularly doped in poly[9-(2,3-epoxypropyl)carbazole] as a host were prepared and photophysical characterization of the individual components and of the molecular mixtures was performed.

2. Experimental

2.1. Instrumentation

¹H NMR and ¹³C NMR spectra were recorded using a Varian Unity Inova (300 MHz and 75.4 MHz) apparatus. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. IR spectra were recorded using a PerkinElmer FT-IR System. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyser. Differential scanning calorimetry (DSC) measurements were carried out using a PerkinElmer DSC thermal analyzer. The DSC

* Corresponding author. Fax: +370 37 300152.

E-mail address: juozas.grazulevicius@ktu.lt (J.V. Grazulevicius).

experiments were performed in a nitrogen atmosphere at a heating rate of 10 °C/min. Melting points (Mp) of the materials were measured using Electrothermal Mel-Temp apparatus. Thermogravimetric analysis (TGA) was performed on Mettler Toledo TGA/SDTA 851^e under nitrogen atmosphere at a heating rate of 20 °C min⁻¹. The ionization potentials (I_p) of the films of the synthesized compounds were measured by electron photoemission in air [22]. The materials were dissolved in chloroform and coated onto Al plates precoated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The function of MKM layer is not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. In addition, this layer is conductive enough to avoid charge accumulation on it during the measurements. Charge transport properties were investigated using time of light (TOF) technique. The samples for the TOF measurements with the structure of ITO/synthesized dyes (~3.2 μm)/Al(60 nm) were prepared by vacuum deposition under the vacuum of 1–3 × 10⁻⁶ mBar. The active area of the fabricated samples was 6 mm². A third harmonic of pulsed Nd:YAG laser (EKSPLA NL300, a wavelength of 355 nm, pulse duration 3–6 ns) was used for the photoexcitation. External bias voltages were applied to the samples by a Keithley 6517B electrometer. The positive or negative polarities of the external bias voltage with respect to the illuminated electrode were identified if the photogenerated holes or electrons were transported through the layers. The photocurrent transients at the different electric fields were measured across a load resistor by the Tektronix TDS 3052C oscilloscope. The transit time (t_{tr}) was determined at the time where the change of the slope in the photocurrent transients was observed. The charge carrier mobility μ was calculated by the relation $\mu = d^2/Vt_{tr}$, where d is the thickness of the layer and V is the applied voltage to the electrodes. The 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 (TBAHFPF₆) as electrolyte, Ag/AgNO₃ as the reference electrode, and a Pt wire counter electrode. The experiments were calibrated with the standard ferrocene/ferrocenium redox system (in our case E_{Fc/Fc^+} vs Ag/Ag⁺ = 0.30 V) [23]. The ionization potentials and electron affinities were calculated by a procedure adopted by Daub, Pommerehne *et al.* based on the value of -4.8 eV for Fc with respect to zero vacuum level [24]. Absorption spectra were recorded on the spectrophotometer Specord UV-vis, luminescence, phosphorescence and luminescence excitation spectra were recorded on the spectrofluorometer Cary Eclipse (Varian) at 293 K and at 77 K. Low-temperature measurements were performed using nitrogen cryostat Optistat DN (Oxford instr.). Luminescence integral quantum yield of the dyes were evaluated by the comparison method. Anthracene solution in ethanol was used as standard solution [25]. 1,4-Dioxane was used as a solvent for the preparation of the solutions as well as for the preparations of the films. The

films were prepared by spin-coating with the following drying at 60 °C in air. The spectra of the films were measured at ambient atmosphere and room temperature. CIE color coordinates were used in the frame of 1931 year standard [26,27]. CRI index was obtained according the method (and software) proposed by Ohno and co-workers [28,29] (because of software specification CRI was obtained from the 380–780 nm range of the luminescence spectrum). The quantum yields of the films were estimated using FLS980 (Edinburgh Instruments Ltd.) equipped with integrating sphere.

2.2. Chemicals

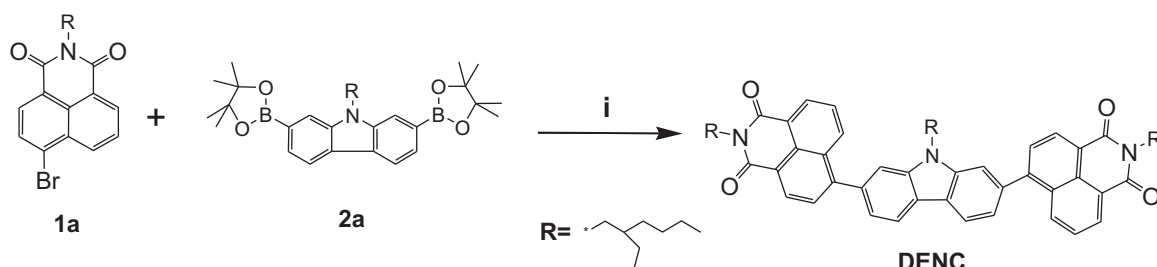
All chemicals and reagents were used as received from commercial sources without further purification. Poly[9-(2,3-epoxypropyl)carbazole] (PEPCa) was purchased from Biolar (Latvia).

2.3. Synthesis

4-Bromo-*N*-(2-ethylhexyl)-1,8-naphthalimide (**1a**) [30], 9-(2-ethylhexyl)-2,7-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-9*H*-carbazole (**2a**) [31], 2,7-di((*N*-(2-ethylhexyl)-1,8-naphthalimide-4-yl)-9,9-di(2-ethylhexyl)-9*H*-fluorene (DEFN) [32], 2-[4-(diphenylamino)phenyl]-1-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (DPPB) [33] were prepared by the described procedures.

2.4. 2,7-Di((*N*-(2-ethylhexyl)-1,8-naphthalimide-4-yl)-9-(2-ethylhexyl)-9*H*-carbazole (DENC)

4-Bromo-*N*-(2-ethylhexyl)-1,8-naphthalimide (**1a**) (0.47 g, 1.21 mmol) and 9-(2-ethylhexyl)-2,7-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-9*H*-carbazole (**2a**) (0.30 g, 0.55 mmol) were taken in a 100 mL Schlenk flask to which a solvent mixture of 20 mL of tetrahydrofuran (THF) and 2 mL of water was added. Powdered potassium carbonate (1.13 g, 8.19 mmol) was added and the reaction mixture was purged with nitrogen for 5 min. The reaction flask was degassed and then, again purged with nitrogen for 2 min. Bis(triphenylphosphine) palladium(II) dichloride (Pd(Ph₃)₂Cl₂) (0.02 g, 0.03 mmol) was added into it and stirred for 16 h at 80 °C under nitrogen. The reaction mixture was allowed to cool down to the room temperature, diluted with water and extracted with ethyl acetate. The organic layers were dried over sodium sulphate and evaporated at reduced pressure. The product was purified by silica gel column chromatography using using an eluent mixture of hexane and ethyl acetate in a volume ratio of 10:1 to obtain DENC as yellow crystals. Yield = 62% (0.12 g); (FW = 910.26 g/mol); M.p. = 124–125 °C. ¹H NMR spectrum (300 MHz, CDCl₃, δ , ppm): 8.75 (d, 2H, $J = 7.5$ Hz, -H_{Naphthalimide}), 8.71 (dd, 2H, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, -H_{Naphthalimide}), 8.65 (dd, 1H, $J_1 = 1.2$ Hz, $J_2 = 7.2$ Hz, -H_{Naphthalimide}), 8.46 (d, 1H, $J = 1.2$ Hz, -H_{Naphthalimide}), 8.43 (d, 1H, $J = 1.1$ Hz, -H_{Naphthalimide}), 8.36 (d, 2H, $J = 7.9$ Hz, -H_{Naphthalimide}), 8.26 (dd, 1H, $J_1 = 1.1$ Hz, $J_2 = 8.28$ Hz,



Scheme 1. The synthetic route to DENC. Reagents and conditions: (i) Pd(Ph₃)₂Cl₂, K₂CO₃, THF/H₂O, N₂ atmosphere, 80 °C, 16–24 h.

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