Journal of Luminescence 130 (2010) 2093–2099

Contents lists available at ScienceDirect

Journal of Luminescence

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

Some spirobiindane based 1*H*-pyrazolo [3,4-*b*] quinoline chromophore as novel chromophore for light-emitting diodes

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ARTICLE INFO

Article history:
Received 30 March 2010
Received in revised form
19 May 2010
Accepted 27 May 2010
Available online 2 June 2010

Keywords:
1*H*-pyrazolo [3,4-*b*] quinolines
Electroluminescence
OLED
Spiro-compounds

ABSTRACT

An influence of phenoxy groups for the luminescent and electroluminescent properties of spiro-compounds with pyrazolo [3,4-*b*] quinoline structure (fluorophore) chromophore has been studied. All the compounds exhibit strong fluorescence in solution and in solid state as well. The prepared compounds were used as dopant chromophore in PVK polymer matrices for electroluminescent (EL) and light-emitting diode (LED) devices with configuration ITO/PEDOT-PSS/PVK/PQ/Ca/Al. Role of the bathochromic shifts and solvent polarity in absorption and photoluminescent maxima is considered. Relation between the number of pyrazoloquinoline chromophore and presence of phenyl group on the fluorescence spectra is explored. Polarizability of the particular pyrazoloquinoline compounds on the solvatochromic effects is investigated. Possible ways of enhancement of the brightness in the light-emitting properties of the mentioned chromophore are discussed.

1. Introduction

The manufacturing of blue luminophors for organic light-emitting diodes (OLED) fabrication requires effective chromophore possessing high light-emitting efficiencies. Molecular luminophors are embedded into a thin film form (basic element of an OLED structure) either through vacuum thermal evaporation or are confined in a host polymer which in turn is spin-coated over appropriate substrate. The confinement can be performed by physical dispersion or alternatively by chemical substitution as a side group. In all the cases high thermal stability is required and it is crucial to avoid crystallization of the titled materials to ensure good working performance of the OLED. This problem is typical for all the luminophores, including the inorganic ones [1].

There were many efforts during recent years in developing *cardo*-, *tetrahedral*-, and *spiro*-systems (both in molecular and polymerized forms) fulfilling the above described requirements. These systems are characterized by elevated temperatures of glass transition, melting, and decomposition [2,3]. The most promising materials were based on spirobifluorene (SBF—Fig. 1(a)) [4–7]. For example spiro-TAD (2,2′, 7,7′-tetrakis-(diphenylamino)-9,9′-spirobifluorene) was used in organic light-emitting diodes (OLED) for hole transport and emitting layer providing violet light [8,9]. This efficient hole conductor was also applied successfully in organic solar cells [10]. It was discovered that three dimensional structures tend to minimize the inter-chain interaction in the polyspirobifluorene which prevents aggregate formation and defect groups, leading to a higher quantum electroluminescence efficiency and better colour purity in an OLED structure [11].

Relatively, spiro-compounds are less studied, in particularly some spirobiindane and its derivatives (SBI—Fig. 1(b)). So far there were only few examples on application of SBI derivatives in organic electronics [12,13] or in nonlinear optics [14].

The scope of this work is further development of such a kind of chromophore. In particular, the SBI molecule was functionalized with pyrazoloquinoline (PQ—Fig. 1(c)) side groups and was just applied in an OLED structure. Pyrazoloquinolines exhibit intense emission in solution and in the solid state as well [15,16]. The quantum yield found for 4-aryl substituted derivatives was close to unity in different solvents. We also fabricated electroluminescent devices with pyrazolo [3,4-*b*] quinolines in the form of evaporated films, dopants in PVK matrix and as polymers,

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doi:10.1016/j.jlumin.2010.05.033

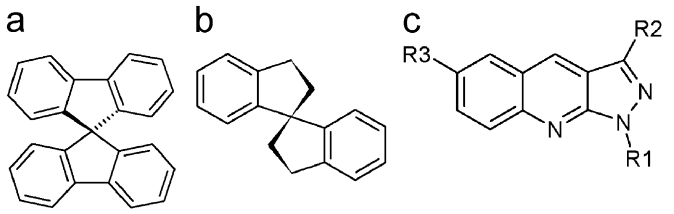


Fig. 1. SBF—spirobifluorene, SBI—spirobiindane, and PQ—pyrazoloquinoline.

respectively [17–20]. Moreover recently Tao et al. applied spirobifluorene 1*H*-pyrazolo [3,4-*b*] quinoline based luminophors for an OLED fabrication [21].

As a consequence in the present work, we study an influence of phenoxy groups for the spiro-compounds possessing pyrazolo [3,4-*b*] quinoline structure (fluorophore). The role of bathochromic shifts for absorption and emission maxima is considered. We investigate the relation between the number of pyrazoloquinolines and presence of phenyl group on the fluorescence spectra. Additionally, polarizability of the particular pyrazoloquinoline compounds on the solvatochromic effects is investigated. Role of solvent polarity on the fluorescence lifetime and red-shift is studied. Possible ways of enhancement of the brightness in the light-emitting properties are discussed.

Technology of synthesis of the studied materials is presented in Section 2. Section 3 describes principal results devoted to absorption and electroluminescent parameters and their discussion.

2. Experimental methods

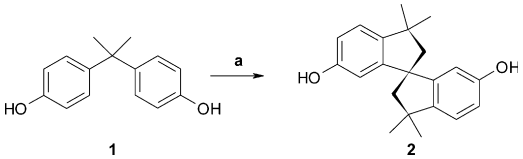
6,6′-dihydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobiindane **2** was prepared from commercially available bisphenol A **1** by heating it in 40% HBr for 12–24 h or by melting with 5 mol% CH_3SO_3H at 135–140 °C [22,23] (Scheme 1). The further reactions are depicted on scheme 2.

Nucleophilic substitution of *p*-fluoronitrobenzene with **2** gave nitroderivative **3** which was reduced to amine **4** with palladium and hydrazine hydrate.

Diamine **4** was heated with 5-chloro-pyrazole-4-carbaldehyde **8** yielding symmetrically substituted SBI with two pyrazoloquinoline moieties. The alternative way of the synthesis is heating of **2** with 6-fluorosubstituted pyrazoloquinolines **6a–d** in the presence of anhydrous K_2CO_3 in an NMP. The unsubstituted 1*H*-pyrazolo [3,4-*b*] quinolines **6i–l,** their 6-phenoxy derivatives **6e–h**, and fluoro-derivatives **6a–d** were prepared in similar way according to the literature procedures [24–26].

All chemicals were purchased from commercial suppliers (Aldrich, Fluka, and POCh) and used as delivered.

^{1}H NMR spectra were recorded on Varian VXR 300 in $CDCl_3$ solution. Melting points were measured in open-end capillaries using a melt-temp II melting point apparatus. The temperatures at the melting points were ramped at 2.5 K/min. Chromatography was performed on column packed with silica-gel (Merck 60, 70–230 meshes). Thin layer chromatography was performed by Merck TLC plates (0.2 mm). Elemental analyses were in a good agreement with the calculated values within ±(0.3–0.4%). The optical absorption spectra were recorded in organic solutions with mass concentration of dyes of about 0.1% for each case. The measurements were performed by means of Shimadzu UV–vis 2101 scanning spectrophotometer in the range 230–600 nm, using a standard 1 cm path length quartz crucible for absorption spectrometry with spectral resolution 1 nm.



Scheme 1. (a) 40% HBr/boiling or CH_3SO_3H 5 mol%/135–140 °C.

The steady state fluorescent emission measurements were performed using a conventional spectrometer with cooled photomultiplier EMI 955 8B operating in single photon counting mode with spectral resolution about 0.8 nm. For excitation, the 365 nm Hg spectral line was used. The fluorescence spectra were renormalized by spectral sensitivity of the detecting system. Samples (prepared in the dark) were degassed before experiments using the freezing–pumping–thawing technique. The fluorescence quantum yields were determined using quinine sulphate in 0.01 H_2SO_4 (Φ_{fl}=0.51) as reference. The fluorescence lifetimes were estimated from decay curves measured by time-resolved single photon counting. As an excitation source, a picoseconds diode laser (λ=400 nm, 70 ps pulse duration) from IBH-UK was applied.

2.1. 6,6-Bis (*p*-nitrophenoxy)-3,3,3′,3′-tetramethyl-1,1′-spirobiindane **3**

SBI **2** (3.1 g, 0.01 mol), p-fluoronitrobenzene (3.5 g, 0.025 mol), anhydrous K_2CO_3 (2.76 g, 0.02 mol), and NMP (20 mL) were heated in a round-bottomed flask (50 mL) at 120 °C for 5 h. The reaction mixture was poured into ice/water mixture and neutralized with 10% HCl. The precipitate was filtered off, dried, and crystallized from EtOH.

Light yellow crystals, 4.9 g, 88%, mp 188–189 °C.

^{1}H NMR (300 MHz, $CDCl_3$, δppm): 8.16–8.10 (m, 4H); 7.19 (d, J=8.2 Hz, 2H); 6.95–6.90 (m, 6H); 6.54 (d, J=2.2 Hz); 2.33 (AB, J_{AB}=13.2 Hz, 4H); 1.40 (s, 6H); 1.39 (s, 6H).

2.2. 6,6-Bis (4-aminophenoxy)-3,3,3′,3′-tetramethyl-1,1′-spirobiindane **4**

6,6-Bis (4-nitrophenoxy)-3,3,3′,3′-tetramethyl-1,1′-spirobiindane (3.3 g, 6 mmol) and palladium(II) chloride on charcoal (20 mg) were suspended in 80 ml of ethanol. The mixture was heated to 80 °C and 20 ml of hydrazine hydrate (80%) was added dropwise with stirring. Then the reaction mixture was heated under reflux for an additional 28 h. Hot reaction mixture was then filtered through Celit and cooled. White precipitate was filtered off and recrystallized from ethanol to give 1.85 g (63%) of gray powder, mp 215–216 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ[ppm]: 1.33 (s, 6H), 1.35 (s, 6H), 2.23/2.34 (AB, J=13.1 Hz, 4H), 2.79 (broad s, 4H), 6.46 (d, J=2.3 Hz, 2H), 6.60–6.65 (m, 4H), 6.73–6.81 (m, 6H), 7.03 (d, J=8.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm]: 30.4, 31.8, 42.9, 57.6, 59.6, 113.9, 116.4, 116.9, 119.9, 122.5, 141.5, 146.5, 150.0, 152.0, 157.6.

2.3. 6,6-Bis(1,3-dimethyl-1H-pyrazolo [3,4-b] quinolin-6-oxy)-3,3,3′,3′-tetramethyl-1,1′-spirobiindane ***5a***—general procedure

Compounds **4** (690 mg, 1 mmol) and **8** ($R^{1,2}$=Me; 320 mg, 2 mmol) were heated together between temperature range 140 and 190 °C for 45 min. The reaction was finished when the liberation of HCl stopped (indicator paper). The melt was dissolved in $CHCl_3$ and filtered through a short pad of aluminium oxide to remove tars. An analytical sample was purified by