Low molecular amorphous spirobifluorene derivatives for blue electroluminescence

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Abstract

We report the synthesis and characterization of new alkoxy substituted spirobifluorene derivatives. The spiro compounds having alkoxy hydrocarbon chains were readily soluble in common organic solvents, having improved film-forming properties and had a significantly reduced tendency to crystallize, resulting in increasing their service lifetime. The results of DSC showed that it was amorphous. The optical and electroluminescent spectra were characterized. Electroluminescence (EL) properties of three-layer light emitting diodes (LED) of ITO/TPD/spirobifluorene/Alq_3/LiF/Al as the active layer were characterized. Blue emission peaking of the EL spectrum of the three-layer device at 402 nm and a luminance of 3,125 cd/m^2 were achieved at a drive voltage 12.8 V. The luminous efficiency was obtained to be 1.7 lm/W. The color coordinate in CIE chromaticity is (0.16, 0.09), which is in a pure blue region. The external quantum efficiency was obtained to be 2.0%. The results indicate that the spirobifluorene compounds having alkoxy hydrocarbon chains are strongly potential blue emitters for LED applications.

Introduction

Organic electroluminescent materials have recently attracted much interest due to their physical properties and potential applications in light-emitting device and flat panel displays. To develop a blue electroluminescence emitter is essential for the development of a full color display based on the color changing medium technology or the RGB filtered white emission [1].

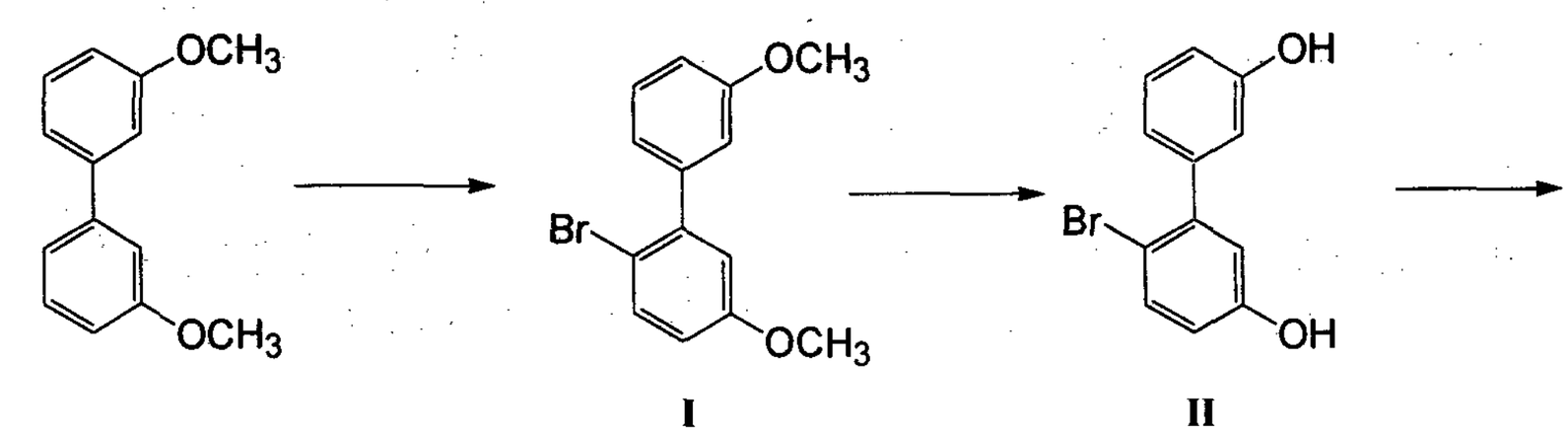
A number of blue electroluminescent materials have been found. J. M. Tour describes polyphenylenes [2]. Even though the good mechanical and thermal properties of the polyphenylenes are known, the insolubility in organic solvents and the associated unsatisfactory processibility and also the instability of doped polyphenylenes greatly impairs commercial utilization. Disadvantages of these low-molecular-weight organic materials are, for example, the unsatisfactory film-forming properties and a pronounced tendency to crystallize.

In addition, a fluorene, planar structure of phenylene, is one of the choice for the blue [3]. However, fluorene derivatives having polar substitutes show an excimer to give a color impurity [4].

Therefore, it is desirable to find EL materials which have no eximer phenomena at solid states and at the same time can be processed into thin homogeneous films which have a low tendency to crystallize. The development of new directions that can lead to stabilization of the amorphous state is a key issue for obtaining pure and stable blue emission. In this way, nonplanar molecular structure has been introduced. C. Hosokawa introduced the blue electroluminescence from 1, 4-bis(2, 2-diphenylvinyl)biphenyl (DPVBi), which is distyrylarylene (DSA), including DSA amine dopant [5].

In a search of another molecular structure, spiro compounds, in particular derivatives of 9,9'-spirobifluorene, have been very suitable as EL materials. Spiro-annulated molecules utilize the spiro-bridge to connect two conjugated moieties. The tetrahedral bonding atom at the center of a spiro-annulated molecules maintains a 90° angle between the connected conjugated moieties via a sigma-bonded network. This structural feature minimizes the close packing of spiro-annulated molecules in the solid state, resulting in reducing the formation of excimer.

A series of 9,9'-spirobifluorene monomer



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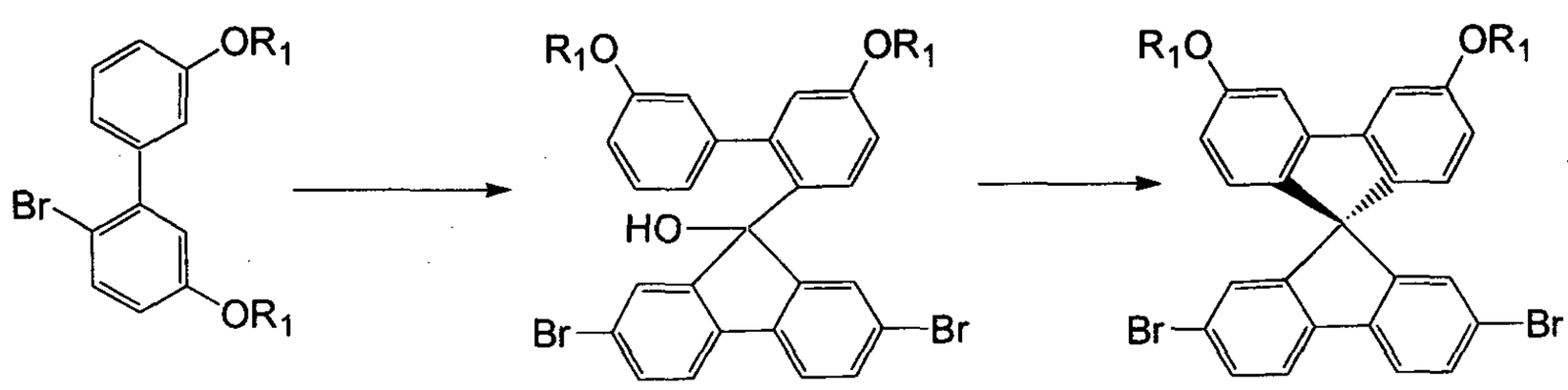

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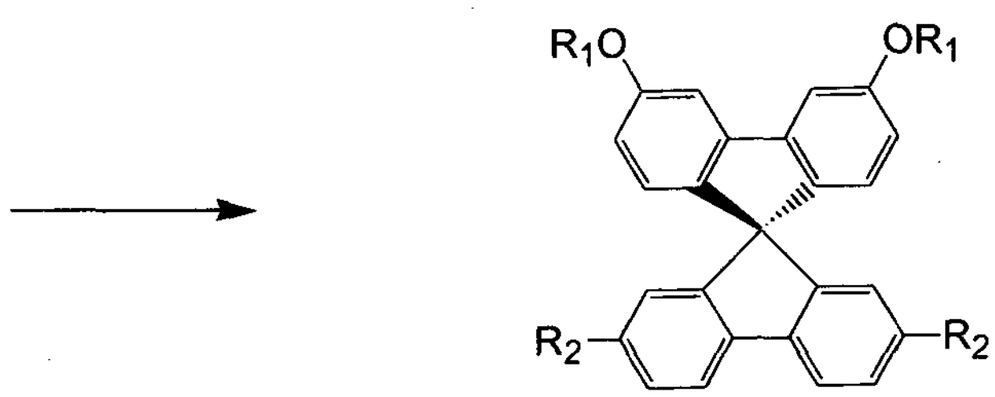

VI

Scheme 1. The synthesis of alkoxy substituted spirobifluorene derivatives.

derivatives has been known [6]. However, their solubility in customary organic solvents is low, especially for high-molecular-weight compounds, even though their thin films of monomers were demonstrated to be amorphous with high T_g and good optical properties.

For an effort to overcome disadvantages of blue EL materials mentioned above, we had designed and synthesized new spirobifluorene compounds having alkoxy hydrocarbon chains.

There are several motifs to design spirobifluorene molecular structure having alkoxy hydrocarbon chains. Molecular interactions of spirobifluorene itself will be diminished to give much less aggregation, resulting in less excimer formation in comparison of alkyl fluorene based compounds known as a blue electroluminescent emitter.

In order to shift blue emission peaking of spirobifluorene to longer wavelength, we introduced alkoxy groups as an electron-donating group to a para-position of spirobifluorene aromatic ring.

The photoluminescence (PL) in solution/film and electroluminescence (EL) spectrum in film are reported in Figure 1.

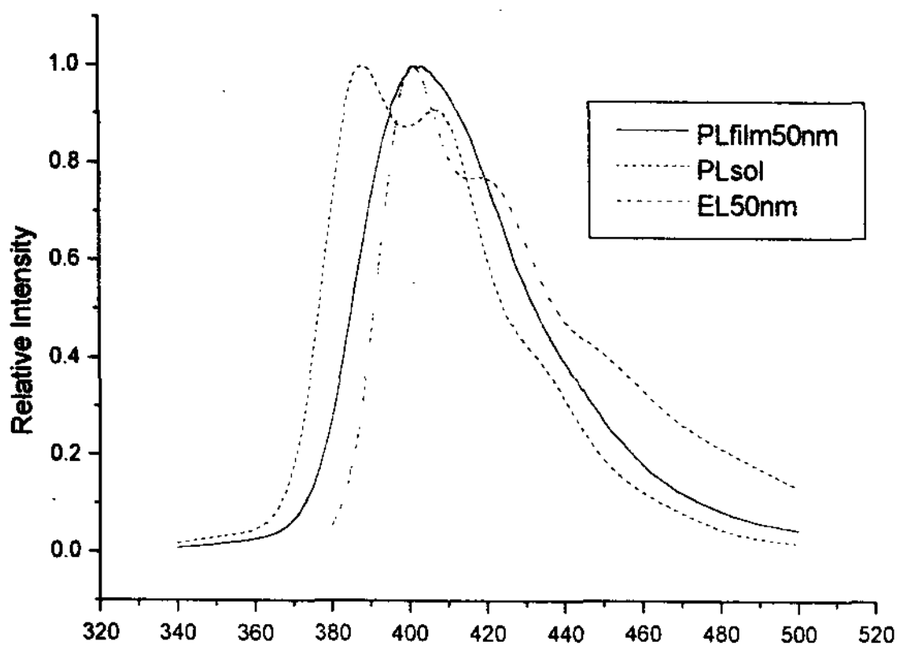

Fig. 1. PL and EL of alkoxy substituted spirobifluorene.

In addition, we expect that the alkoxy group should help to give much better solubility than only phenyl substituted one of spirobifluorene [7]. In fact, the alkoxy-substituted spirobifluorene compounds were readily soluble in common organic solvents,

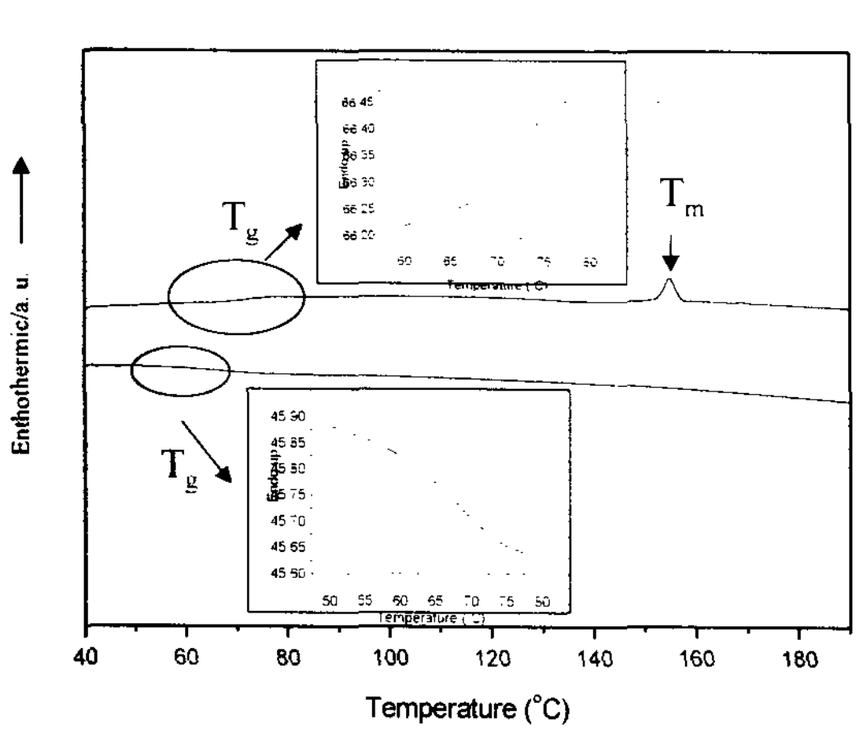

Fig. 2. The DSC data on heating at 10 °C /min and cooling in air

having improved film-forming properties and had a significantly reduced tendency to crystallize, resulting in increasing their service lifetime.

The detailed synthesis of spirobifluorene derivatives is shown in scheme 1.

All the compounds had been fully characterized by ^{1}H NMR, UV-VIS, IR, and mass spectrometry and gave satisfactory elemental analyses.

Differential scanning calorimetry (DSC) performed on a crystalline sample showed that upon heating, it melted at 168 °C to give an isotropic liquid. When the isotropic liquid was cooled on standing in air, it formed a transparent, stable amorphous glass via supercooled liquid state. The glass transition temperature (T_g) was about 70 °C on heating and about 60 °C on cooling. When the sample was heated again, the glass transition temperature was not changed a lot. The glassy state of this material is very stable, no crystallization being observed. The DSC data are reported in Fig. 2.

We can investigate properties of three-layer light emitting diodes of ITO/TPD/spirobifluorene (BO-6p)/Alq_3/LiF/Al as a primary result. Blue emission peaking of the EL spectrum of the three-layer device at 402 nm as shown in Fig. 1 and a luminance of 3,125 cd/m^2 were achieved at a drive voltage 12.8 V as shown in Fig. 3.

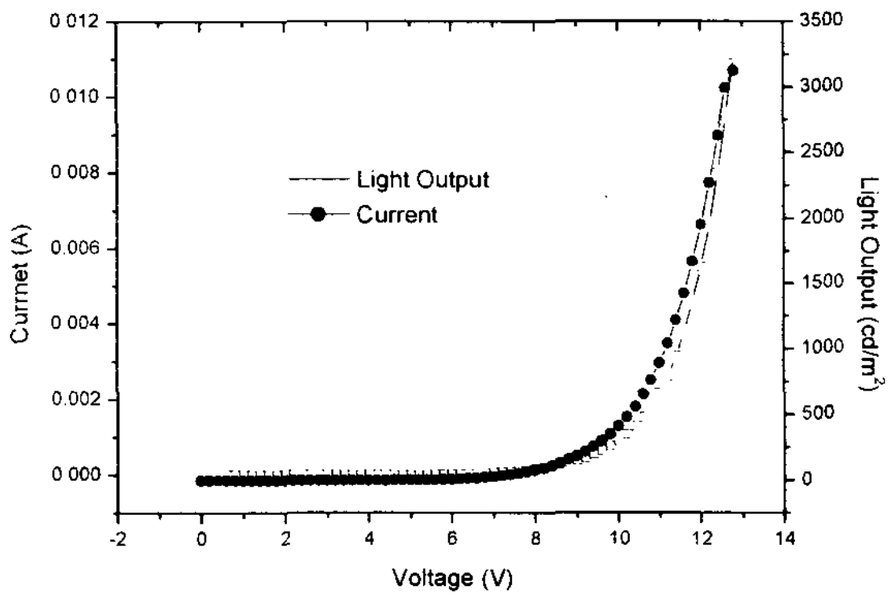

Fig. 3. I-V-L curve of alkoxy substituted spirobifluorene.

The luminous efficiency was obtained to be 1.7 lm/W. The color coordinate in CIE chromaticity is (0.16, 0.09), which is in a pure blue region. The external quantum efficiency was obtained to be 2.0 %.

In this report, the more detailed studies about the synthesis and characterization and its LED device will be discussed.

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