Bright oligothiophene-based light emitting diodes

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Abstract

We demonstrate bright and efficient spin-coated yellow organic light emitting diodes (OLEDs) employing as active medium a novel thiophene-based compound, in which the conventional linear structure of the oligothiophenes has been replaced by a branched benzo[*b*]thiophene-based structure. Such a structure, combined with the oxygen functionalization of the core-thienyl sulphur atom and the cyclohexyl substitution of the lateral thienyl rings, allowed us to obtain a brightness up to 10,500 cd/m² and an external quantum efficiency up to 0.48%, which are the highest values so far obtained by substituted oligothiophene-based compounds.

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Keywords: OLED; Oligothiophenes; Quantum yield

1. Introduction

In the last decade, electroluminescent conjugated molecules have been the subject of intense research, aiming at their application to light emitting diodes [1,2] and displays with high efficiency [3], brightness [4] and low operating voltage. In this frame, thiophene derivatives are relevant due to their high chemical stability [5], full color tunability [6] and high processability. In particular, in such compounds the photoluminescence (PL) efficiency in the solid state can be strongly affected by the packing effects, which can be controlled by a proper functionalization of the structure [6,7]. For instance, functionalising the thienyl sulphur atom by two oxygen atoms has been demonstrated to introduce novel polar intermolecular interactions which can disrupt the typical Herring-Bone (HB) supramolecular organization of unsubstituted oligothiophenes, thus strongly increasing the luminescence efficiency [7]. Moreover, the intermolecular non-radiative decay channels could be further reduced by grafting large volume groups (such as cyclohexyls) at the β positions of the thienyl rings, thus increasing the steric hindrance and separating the molecules.

In this work, we report on a novel, highly efficient and processable yellow-emitting thiophene-based compound,

BToCx, in which both the oxygen and cyclohexyl functionalizations are made on a branched benzo[*b*]thiophene-based structure. This compound was used as the active medium of organic light emitting diodes (OLEDs). The achieved electroluminescence (EL) performances (brightness up to 10,500 cd/m² and EL quantum efficiency up to 0.48%) are the best so far obtained for substituted thiophenes-based compounds.

2. Experimental

The molecular structure of BtoCx is reported in the inset of Fig. 1. PL and PL efficiency measurements were carried out on thin films, spin-cast from chloroform solution (10^{−2} M), by using an integrating sphere [8] and exciting the samples by a He–Cd laser ($\lambda = 325$ nm). Absorption (Abs) spectra were recorded by an UV–Vis spectrophotometer (Varian Cary 100-Scan). All measurements were carried out under a continuous N₂ flux to inhibit photo-oxidation.

The light emitting devices were fabricated by spin-coating the active material onto indium tin oxide (ITO)-coated glass substrates preliminarily treated by oxygen plasma. In order to improve the OLED performances, we spin-cast a 100-nm thick hole-transporting layer, namely poly(3,4-ethylene dioxythiophene) (PEDOT) doped by poly(styrene sulphate) (PSS) between the ITO and the active layer. Finally, the cathode (Al-capsulated Ca—100 nm) was deposited on the active medium by thermal evaporation at 10^{−4} Pa.

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The active area of the devices, given by the overlap of the cathode and the ITO electrode, was 4 mm^2 . The device characterization was performed in air atmosphere.

3. Results and discussion

The room temperature PL and the Abs spectra of BToCx in the solid state are shown in Fig. 1. The absence of a well-defined vibrational structures in both spectra, suggesting a broad distribution of ground and excited-state molecular conformations, is consistent with a high degree of structural disorder. This is enhanced by the steric hindrance introduced by the cyclohexyl groups and by the non linear structure of our compound. The measured PL efficiency, as high as 21%, is consistent with the increased distance between molecules, and the consequent suppression of non-radiative decay channels related to strong intermolecular interactions.

The current density and the luminance of our OLEDs versus the applied voltage are shown in Fig. 2. The EL

Fig. 1. Absorption and PL spectra of BToCx. Inset: chemical structure of BToCx.

Fig. 2. Luminance and current density vs. applied voltage of BToCx-based OLEDs.

Fig. 3. EL efficiency vs. applied voltage of BToCx-based OLEDs. Inset: EL spectrum.

emission of BToCx is reported in the inset of Fig. 3. The device characteristics are quite good over the entire of bias, exhibiting a maximum brightness of $10,500\text{ cd/m}^2$. The EL efficiency reaches values as high as 0.48% (Fig. 3), that is almost five times larger than the best results previously reported for substituted oligothiophenes [9]. This is a consequence of the excellent luminescence performances and film forming properties of BToCx, and of the good carrier injection towards the active material from the PEDOT-PSS and from the calcium electrode, as found for other oxygen substituted thiophene-based compounds [6–8]. Finally, we underline that the device characteristics show very good stability for a few hours of operation in air.

4. Conclusion

In conclusion, we presented a new highly processable oligothiophene-based compound, with a branched molecular structure based on a oxygenated benzo[b]thiophene core and two cyclohexyl functionalized thienyl chains. This molecule exhibits very good PL efficiency (21%), EL luminance ($10,500\text{ cd/m}^2$) and efficiency (0.48%), in air atmosphere. All these characteristics make this oligothiophene an excellent candidate for display technologies.

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