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Synthesis and characterization of new electroluminescent molecules containing carbazole and oxadiazole units

Valeria Bugatti[a], Simona Concilio[a], Pio Iannelli[a,*], Stefano P. Piotto[a], Salvatore Bellone[b], Manuela Ferrara[b], Heinrich C. Neitzert[b], Alfredo Rubino[b], Dario Della Sala[c], Paolo Vacca[c]

[a] Dipartimento di Ingegneria Chimica ed Alimentare, Università di Salerno, via Ponte Don Melillo, I-84084 Fisciano (Salerno), Italy
[b] Dipartimento di Ingegneria Elettronica, Università degli Studi di Salerno, via Ponte Don Melillo, I-84084 Fisciano (Salerno), Italy,
[c] ENEA C.R. Portici, v. Vecchio Macello-loc. Granatello, 80055 Portici (Na), Italy

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Abstract

The synthesis of new molecules containing both electron and hole transporter units is reported. This class of compounds, named **OC**, may be used for assembling electroluminescent devices made by a single organic layer. The active moieties are the carbazole, as the hole transporter unit, and the oxadiazole, as the electron transporter unit. The chemical formulation and the complex geometry of the molecular frame allow good solubility in chlorinate solvents and the preparation of homogeneous films by spinning technique.

Photoluminescence of molecules, both in solution and in film, occurs in the blue region of visible spectra, the exact peak position of emission depending on the pendants attached to the oxadiazole unit. The electroluminescence occurs in a higher wavelength region, with a blue-green emission. The electroluminescent devices consist in the simple sequence ITO–**OC**–Al and ITO–PEDOT–**OC**–Al.

Keywords: Electroluminescent molecules; Carbazole; Oxadiazole; Single layer oled

1. Introduction

In the last years a number of new low molecular mass compounds and polymeric materials have been synthesized and analyzed for applications in the field of organic light-emitting devices (OLEDs) [1–12]. For fabricating a LED it is usually required the presence of very thin layers of both hole-transporting and electron-transporting molecules. The two layers are confined between a hole-injection electrode and a low work function electron-injection metal contact, respectively. Electroluminescence is induced by the recombination of holes and electrons, when the resulting diode is biased in forward direction.

The use of a single layer in the preparation of OLEDs is attractive for the easier technology approach, the less expensive application of only a single thin layer and the suppression of the interface between the two-layers [13–17]. Multi-layer devices are difficult to produce by spin-coating of the organic molecules, because the solvent used for the spinning of a second layer will generally dissolve also the previously deposited layers. Oppositely, single layer has been considered less promising for the lower luminous efficacy because the balance between hole and electron current is more difficult to control.

To prepare a single layer system it is necessary to include both the active moieties, hole and electron transporting, in the layer composition. This may be obtained by mixing the two components, but problems may occur due to physical separation and crystallization of components. A way to ensure high stability of composition is to chemically bond the two moieties, thus imposing a chemical constraint, which avoids any segregation and suppresses crystallization. Moreover, the chemical linkage may be chosen in order to tailor solubility, morphology and other properties of the active molecules.

We have recently shown that new oxadiazole-containing compounds are blue-photoluminescent materials [18,19], in agreement with that reported by several authors for similar

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[*] Corresponding author. Fax: +39 089 964 057.
E-mail addresses: piannelli@unisa.it, Iannelli@dica.unisa.it (P. Iannelli).

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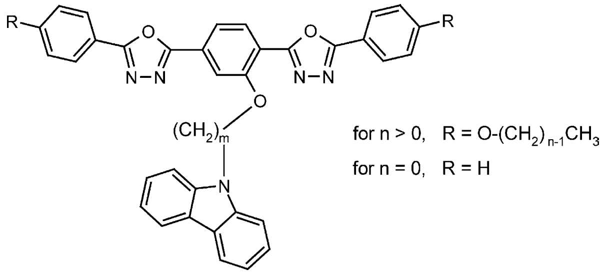
molecules [20–32]. We observed that the anisotropic shape of conjugated unit promotes the appearing of high ordered smectic phases and, only in few cases, of the nematic phase. The liquid crystalline (LC) order is particularly interesting when optical active systems are required to be anisotropic at the macroscopic level.

In this paper, we report on the synthesis and the characterization of a new class of photo- and electroluminescent molecules having formula:



OC (n,m)

The insertion of the flexible aliphatic segments along and side attached to the aromatic molecular frame moderates melting temperature and promotes solubility in common organic solvents.

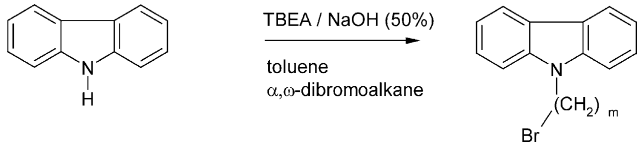
Electroluminescence and optical properties of OLEDs made by using **OC** as single layer component is also reported and discussed.

2. Experimental

2.1. Materials

All reagents and solvents were purchased from Aldrich and Carlo Erba. *N*,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylformamide (DMF) were refluxed on calcium hydride, distilled in vacuum and stored on 4 Å molecular sieves. Other reagents were used without further purification. *n*-Alkoxybenzylchloride, *n*-alkoxyterephthalic acid and its methyl ester derivative were synthesized according to a previously reported procedure [33,34].

2.1.1. Synthesis of N-(4-bromobutyl)carbazole

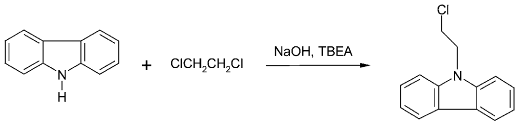


Following the procedure described in reference [35], a suspension of carbazole (0.0870 mol) and 1,4-dibromobutane (0.261 mol) in 60 ml of toluene was added to 44 ml of aqueous solution of benzyltriethylamonium bromide (TBEA, 0.00362 mol) in 50% aqueous NaOH, and the reaction was led to take place for 20 h, at room temperature.

The final mixture was poured into 600 ml of distilled water and the product extracted twice with 150 ml of chloroform. The organic layer was subsequently washed twice with 300 ml of water, dried over sodium sulfate and the solvent was removed at reduced pressure. The row amber-yellow product was purified by treatment in boiling *n*-heptane (200 ml), to remove the excess of 1,4-dibromobutane. The white solid product collected at room temperature was then crystallized form ethanol/water. The *N*-(4-bromobutyl)carbazole was obtained as needle crystalline solid, with a 50% yield. $T_m = 103.33\,^{\circ}C$; $\Delta H_m = 75.231$ J/g.

^{1}H NMR ($CDCl_3$): δ (ppm) = 8.15 (d, 2H), 7.46 (m, 4H), 7.29 (m, 2H), 4.33 (t, 2H), 3.40 (t, 2H), 2.05 (m, 2H), 1.97 (m, 2H).

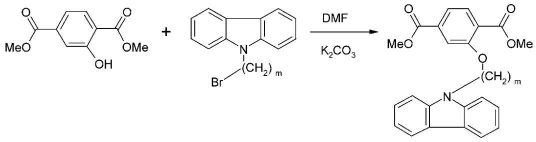
2.1.2. Synthesis of N-(2-chloroethyl)carbazole



Following the procedure described in reference [36], in a 100 ml round bottom flask, to a solution of carbazole (0.059 mol) in 1,2-dichloroethane (1.256 mol), TBEA (0.0020 mol), and NaOH 16 M (35 ml) were subsequently added. The mixture was let to react for 12 h, at 60 °C. The reaction mixture was dried under vacuum at 80 °C, and a solid was obtained. This raw product was purified by crystallization from ethanol, to eliminate the insoluble salt, and a second crystallization from *n*-heptane, to isolate the *N*-(2-chloroethyl)carbazole from the unreacted carbazole. The finale product was a needle-shape crystalline solid, obtained with a 30% yield. $T_m = 128.3\,^{\circ}C$, $\Delta H_m = 114.3$ J/g.

^{1}H NMR ($CDCl_3$): δ (ppm) = 8.12 (d, 2H), 7.45 (m, 4H), 7.28 (m, 2H), 4.66 (t, 2H), 3.86 (t, 2H).

2.1.3. Synthesis of 2-(4-carbazol-9-yl-butoxy)-terephthalic acid dimethyl ester (*1*) and 2-(2-carbazol-9-yl-ethoxy)-terephthalic acid dimethyl ester (*2*)



2-Hydroxy-terephthalic acid dimethyl ester (0.0300 mol) was dissolved in 250 ml of DMF; potassium carbonate was added and a solution of *N*-(4-bromobutyl)carbazole or *N*-(2-chloroethyl)carbazole (0.0360 mol) in DMF (50 ml) was added drop wise to the first solution. The mixture was stirred at 150 °C for 16 h and then filtered into water (1200 ml). The aqueous solution was placed at 4 °C for 4 h and the solid crude product was filtered under vacuum and purified by crystallization from ethanol/water. The ester was colleted as pale yellow needles with approximately 70% final yield.

(**1**) $T_m = 112.3\,^{\circ}C$; $\Delta H_m = 55.2$ J/g; ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.09 (d, 2H), 7.74 (d, 1H), 7.68 (s, 1H), 7.62 (d, 1H), 7.56 (m, 2H), 7.46 (m, 2H), 7.24 (m, 2H), 4.44 (t, 2H), 4.09 (t, 2H), 3.94 (s, 3H), 3.77 (s, 3H), 2.15 (m, 2H), 1.92 (m, 2H).

(**2**) Yellow oil; the compound was used without purification in the following synthesis of the dihydrazide derivative.