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# 3,9'-Bicarbazole-Based Compounds with Reactive Functional Groups as Potential Cross-Linkable High Triplet Energy Hole-Transporting Materials

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# 3,9'-Bicarbazole-Based Compounds with Reactive Functional Groups as Potential Cross-Linkable High Triplet Energy Hole-Transporting Materials

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New oxiranyl-substituted derivatives of 3,9'-bicarbazole were synthesized by synthetic route involving Ullmann coupling, Vilsmeier formylation, reduction with sodium borohydride and the interaction of hydroxymethyl derivatives with 2-(chloromethyl)oxirane. The optical, photophysical and photoelectrical properties of the newly synthesized materials were studied. The electron photoemission spectra of the materials revealed the ionization potentials ranging range from 5.55 to 5.70 eV. Time-of-flight hole drift mobilities of bisphenol Z polycarbonate doped with 50 wt.% 3,9'-bicarbazole -based compounds exceed  $10^{-6}\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ .

**Keywords** Carbazole derivatives; hole drift mobility; ionization potential; oxiranyl functionalized

### Introduction

The efficiencies of organic electrophosphorescent devices have increased significantly recently due to development of efficient phosphorescent guest molecules which can harvest both electro-generated singlet and triplet excitons for emission [1–5]. For efficient electrophosphorescence from triplet guests in a host matrix, the triplet energy of the host has to be larger than that of the guest to facilitate exothermic energy transfer from the host to the guest and to prohibit reverse energy transfer from the guest back to the host (i.e., to effectively confine triplet excitons on guest molecules) [6–8]. Among host materials reported carbazole derivatives prevail [5,8,9]. Carbazole-based materials simultaneously possess large enough triplet energies and are electronically active [10]. An important requirement to hosts and other materials used in organic electroluminescent devices, is their thin film morphological stability. It can be enhanced by increasing molecular size. To acquire sufficient

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thin-film morphological stability in devices, extension of molecular size to obtain bulky and steric molecular configurations is often done. Much more effective tool of increasing thin-film morphological stability can be (photo)cross-linking. For this high triplet energy electroactive molecules with reactive functional groups are required. We have earlier reported that 3,9'-bicarbazoles are effective host materials for efficient blue organic electrophosphorescent devices [9]. In this article we report on the synthesis of 3,9'-bicarbazoles, containing reactive functional groups, which can be regarded as potential cross-linkable high triplet energy hole-transporting materials.

# **Experimental**

#### Instrumentation

<sup>1</sup>H NMR spectra were recorded using Varian Unity Inova [300 MHz (<sup>1</sup>H)] spectrometer. All the data are given as chemical shifts d (ppm) downfield from Si(CH<sub>3</sub>)<sub>4</sub>. IR spectra were recorded using PerkinElmer Spectrum GX II FT-IR System. The spectra of the solid compounds were performed in the form of KBr pellets. Mass spectra were obtained on a Waters ZQ 2000. UV spectra of 10<sup>5</sup> M solutions of the synthesized compounds in THF were recorded on Perkin Elmer Lambda 35 spectrometer. Steady state fluorescence spectra were recorded with Hitachi MPF-4 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out with a Perkin Elmer Pyris Diamond calorimeter. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 aparatus. The TGA and DSC experiments were performed in nitrogen atmosphere at a heating rate of 10°C/min. Melting points were measured on Electrothermal MEL-TEMP melting point apparatus. The ionization potentials (Ip) of the films of the synthesized compounds were measured by electron photoemission in air method as described before [11]. Hole drift mobilities were measured by a xerographic time-of-flight (XTOF) method [12,13]. The samples for the charge carrier mobility measurements were prepared by casting the solutions of the mixtures of the synthesized compounds with bisphenol Z polycarbonate (PC-Z) on polyester films with Al layer [14]. The thickness of the charge-transporting layers varied in the range of 6–7 mm.

### Materials

9H-carbazole, sodium borhydride, potassium hydroxide, 2-(chloromethyl) oxirane, POCl<sub>3</sub> were purchased from Aldrich and used as received.

9-ethyl-3,9'-bicarbazole (1) was prepared by the procedure described earlier [15]. 9-ethyl-3,9'-bicarbazole-3'-carbaldehyde (2a), 9-ethyl-3,9'-bicarbazole-6-carbaldehyde (2b) and 9-ethyl-3,9'-bicarbazole-3',6-dicarbaldehyde (2c) were synthesized by the method of Vilsmeier [16] according to the following general procedure. POCl<sub>3</sub> (2.54 ml, 27.22 mmol) was added dropwise to dry DMF (5.96 ml, 81.66 mmol) at 0°C under nitrogen atmosphere. 9-Ethyl-3,9'-bicarbazole (7 g, 19.44 mmol) was dissolved in 3 g of DMF and the solution was added stepwise to the reaction flask. The reaction mixture was stirred at 85°C. Then the reaction mixture was cooled down to the room temperature, poured into ice water and neutralized with 10% solution of potassium hydroxide till pH = 6-8. The reactions products were extracted with ethyl acetate. The combined organic phase was dried with sodium sulfate, filtered, and concentrated under vacuum. The products were purified by silica gel column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 4:1. The yield of 9-ethyl-3,9'-bicarbazole-3'-carbaldehyde (**2a**) was 1.3 g (19%), the yield of 9-ethyl-3,9'-bicarbazole-6-carbaldehyde (**2b**) was 0.7 g (10%), and that of 9-ethyl-3,9'-bicarbazole-3',6-dicarbaldehyde (**2c**) was 2.1 g (29%).

9-ethyl-3,9'-bicarbazole-3'-carbaldehyde (**2a**) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ , ppm.: 1,52 (t, J=7,2 Hz, 3H, CH<sub>3</sub>); 4,46 (q, J=7,2 Hz, 2H, CH<sub>2</sub>); 7,21–7,63 (m, 9H, ar 1-H, 2-H, 6-H, 7-H, 8-H, 1'-H, 6'-H, 7'-H, 8'-H); 7,92 (dd, J=8,6 Hz, J=1,58 Hz, 1H ar 2'-H); 8,05 (d, J=7,8 Hz, 1H, ar 5-H); 8,18–8,25 (m, 2H, ar 4-H, 5'-H); 8,68 (d, J=1,46 Hz, 1H, ar 4'-H); 10,1 (s, 1H, CHO). IR (KBr) v, cm<sup>-1</sup>: 3048 (C-H ar); 2962, 2925 (C-H alif); 1684 (C=O); 1623, 1597, 1565 (C=C ar); 1241 (C-N). MS(APCI<sup>+</sup>, 20 V), m/z (%):389([M+H]<sup>+</sup>, 60).

9-ethyl-3,9'-bicarbazole-6-carbaldehyde (**2b**)  $^{1}$ H BMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ , m.d.: 1,61 (t, J = 7,2 Hz, 3H, CH<sub>3</sub>); 4,53 (q, J = 7,2 Hz, 2H, CH<sub>2</sub>); 7,29–7,75 (m, 9H, ar 1-H, 2-H, 7-H, 8-H, 1'-H, 2'-H, 3'-H, 6'-H, 7'-H, 8'-H); 8,12 (dd, J = 8,55 Hz, J = 1,4 Hz, 1H ar 7-H); 8,23 (d, J = 7,7 Hz, 2H, ar 4'-H, 5'-H); 8,36 (d, J = 1,80 Hz, 1H, ar 4-H); 8,62 (d, J = 1,4 Hz, 1H, ar 5-H); 10,12 (s, 1H, CHO). IR (KBr) v, cm<sup>-1</sup>: 3051 (C-H ar); 2966, 2928, 2893, 2813 (C-H alif); 1684 (C = O); 1596(C = C ar); 1233 (C-N). MS(APCI<sup>+</sup>, 20 V), m/z (%):389([M+H]<sup>+</sup>, 32).

9-ethyl-3,9'-bicarbazole-3',6-dicarbaldehyde (**2c**) <sup>1</sup>H BMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ , m.d.: 1,62 (t, J = 7,2 Hz, 3H, CH<sub>3</sub>); 4,56 (q, J = 7,2 Hz, 2H, CH<sub>2</sub>); 7,38–7,75 (m, 7H, ar 1-H, 2-H, 8-H, 1'-H, 6'-H, 7'-H, 8'-H); 7,97 (dd, J = 8,5 Hz, J = 1,6 Hz, 1H ar 2'-H); 8,13 (dd, J = 8,6 Hz, J = 1,5 Hz, 1H, ar 7-H); 8,25–8,29 (m, 1H, ar 5'-H); 8,33 (d, J = 1,6 Hz, 1H, ar 4-H); 8,62 (d, J = 1,3 Hz, 1H, ar 4-H); 8,72 (d, J = 1,3 Hz, 1H, ar 4-H); 10,11 (s, 1H, CHO); 10,15 (s, 1H, CHO). IR (KBr) v, cm<sup>-1</sup>: 3051 (C-H ar); 2955, 2924, 2853 (C-H alif); 1685 (C = O); 1622, 1592, 1567, 1494 (C = C ar); 1232 (C-N). MS(APCI<sup>+</sup>, 20 V), m/z (%): 417([M+H]<sup>+</sup>, 100).

9-ethyl-3'-hydroxymethyl-3,9'-bicarbazole (**3a**) was synthesized by the similar procedure to that described earlier [17]. Sodium borohydride (0.09 g, 2.32 mmol) was added by small portions into the solution of 0.75 g (1.93 mmol) of 9-ethyl-3,9'-bicarbazole-3'-carbaldehyde (**2a**) in 200 ml of methanol. The reaction mixture was refluxed for 2 hours and stopped when no starting compounds were observed in the reaction mixture (TLC control). After cooling the reaction mixture was poured into 800 ml of ice water. The precipitated product was separated by filtration. Yield 0,5 g (67%.). <sup>1</sup>H BMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ , m.d.: 1,58 (t, J = 7,2 Hz, 3H, CH<sub>3</sub>); 1,84 (s, 1H, OH); 4,51 (q, J = 7,2 Hz, 2H, I CH<sub>2</sub>-CH<sub>3</sub>); 4,92 (s, 2H, I CH<sub>2</sub>-OH); 7,26–7,64 (m, 10H ar 1-H, 2-H, 6-H, 7-H, 8-H, I 1'-H, 2'-H, 6'-H, 7'-H, I 8'-H); 8,08–8,13 (m, 1H, ar 5-H); 8,20–8,25 (m, 2H, ar 4'-H, 5'-H); 8,25–8,28 (m, 1H, ar 4-H). IR (KBr) v, cm<sup>-1</sup>: 3340 (OH); 3047 (=CH ar); 2971, 2927, 2869 (C-H alif); 1626, 1600, 1572 (C=C ar); 1232 (C-N). MS(APCI<sup>+</sup>, 20 V), m/z (%): 391([M+H]<sup>+</sup>, 3).

9-ethyl-6-hydroxymethyl-3,9'-bicarbazole (**3b**) was synthesized by the same procedure as **3a** using 9-ethyl-3,9'-bicarbazole-6-carbaldehyde (**2b**) (0.5 g, 1.29 mmol) and sodium borohydride (0.06 g, 1.54 mmol). Yield 0.34 g (68%). <sup>1</sup>H BMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ , m.d.: 1,57 (t, J = 7,2 Hz, 3H, CH<sub>3</sub>); 1,89 (s, 1H, OH); 4,51 (q, J = 7,2 Hz, 2H, CH<sub>2</sub>-CH<sub>3</sub>); 4,89 (s, 2H, CH<sub>2</sub>- OH); 7,28–7,72 (m, 10H ar 1-H, 2-H, 7-H, 8-H, 1'-H, 2'-H, 3'-H, 6'-H, 7'-H, 8'-H); 8,10–8,21 (m, 1H, ar 5-H); 8,20–8,25 (m, 2H, ar 4'-H, 5'-H); 8,25–8,28 (m, 1H, ar 4-H). IR (KBr) v, cm<sup>-1</sup>: 3332 (OH); 3046 (= CH ar); 2971, 2929, 2868 (C-H alif); 1626, 1601, 1575 (C = C ar); 1232 (C-N). MS(APCI<sup>+</sup>, 20 V), m/z (%): 391([M+H]<sup>+</sup>, 18).

9-ethyl-6,3'-dihydroxymethyl-3,9'-bicarbazole (**3c**) was synthesized by the same procedure as 3a using 9-ethyl-3,9'-bicarbazole-6-carbaldehyde (**2c**) (1 g, 2.4 mmol) and sodium borohydride (0.11 g, 2.88 mmol). Yield 0,76 g (80%). <sup>1</sup>H BMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ , m.d.: 1,54 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); 2,10 (s, 2H, OH); 4,47 (q, J = 7.2 Hz, 2H, CH<sub>2</sub>-CH<sub>3</sub>); 4,86 (s, 2H, CH<sub>2</sub>-OH); 4,89 (s, 2H, CH<sub>2</sub>-OH); 7,28–7,62 (m, 9H ar 1-H,  $\overline{2}$ -H, 7-H, 8-H, 1'-H, 2'-H, 6'-H, 7'-H, 8'-H); 8,07 (d, J = 7.7 Hz, 1H, ar 5-H); 8,17–8,24 (m, 2H, ar 4-H, 4'-H, 5'-H). IR (KBr) v, cm<sup>-1</sup>: 3326 (OH); 3046 (= CH ar); 2972, 2931, 2868 (C-H alif); 1626, 1601, 1577 (C=C ar); 1233 (C-N). MS(APCI<sup>+</sup>, 20 V), m/z (%): 421([M+H]<sup>+</sup>, 2).

9-ethyl-3'-(2-oxiranylmethyl)-3,9'-bicarbazole (4a). 9-Ethyl-3'-hydroxymethyl-3,9'-bicarbazole (3a) (1 g, 2.56 mmol) was dissolved in 10 ml of 2-(chloromethyl)-oxirane. Then powdered potassium hydroxide (0.5 g, 8.93 mmol) and potassium carbonate (0.21 g, 1.48 mmol) were added to the reaction mixture. The reaction was carried out for 24 h at 30°C. Then the reaction mixture was extracted with diethyl ether, and the extract was washed with distilled water. The organic layer was dried with sodium sulfate, filtered, and concentrated to give crude product. The product was purified by silica gel column chromatography using an eluent mixture of hexane and acetone in a volume ratio of 2:1. Yield 0.49 g (52%).

<sup>1</sup>H BMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ , m.d.: 1,58 (t, J=7,2 Hz, 3H, CH<sub>3</sub>); 2,74 (dd, J=5,1 Hz, J=2,7 Hz 1H, one of CH<sub>2</sub>O protons in oxirane ring); 2,9 (dd, J=5,1 Hz, J=4,17 Hz, 1H, CH<sub>2</sub>O another proton in oxirane ring); 3,3–3,37 (m, 1H, CHO); 3,59 (dd, J=11,7 Hz, J=5,8 Hz, 1H, one of CH<sub>2</sub>O protons); 3,91 (dd, J=11,4 Hz, J=3,1 Hz, 1H, CH<sub>2</sub>O another proton); 4,49 (q, J=7,2 Hz, 2H, CH<sub>2</sub>-CH<sub>3</sub>); 4,88 (q, J=11,4 Hz, 2H, ar-CH<sub>2</sub>-O); 7,28–7,7 (m, 10H, ar 1-H, 2-H, 6-H, 7-H, 8-H, 1'-H, 2'-H, 6'-H, 7'-H, 8'-H); 8,10–8,18 (m, 1H, ar 5-H); 8,28–8,31 (m, 2H, ar 4'-H, 5'-H); 8,31–8,35 (m, 1H, ar 4-H). IR (KBr): 3047 (CH ar), 2973, 2929, 2866 (CH alif), 1625, 1598, 1571 (C=C ar), 1232 (C-N), 900, (C-O in oxirane ring). MS(APCI<sup>+</sup>, 20 V), m/z (%): 447([M+H]<sup>+</sup>, 2).

9-ethyl-6,3'-di(2-oxiranylmethyl)-3,9'-bicarbazole (**4b**) was synthesized by the same procedure as **4a** using 9-ethyl-6,3'-dihydroxymethyl-3,9'-bicarbazole (**3c**) (1 g, 2.56 mmol), potassium hydroxide (1 g, 17.86 mmol) and potassium carbonate (0.42 g, 2.96 mmol). Yield 0.68 g (49%). <sup>1</sup>H BMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ , m.d.: 1,58 (t, J=7,2 Hz, 3H, CH<sub>3</sub>); 2,70 (dd, J=5,1 Hz, J=2,7 Hz 2H, one of CH<sub>2</sub>O protons in oxirane ring); 2,87 (dd, J=4,2 Hz, J=9,9 Hz, 2H, CH<sub>2</sub>O another proton in oxirane ring); 3,25–3,31 (m, 2H, CHO); 3,56 (dd, J=11,4 Hz, J=5,8 Hz, 2H, one of CH<sub>2</sub>O protons); 3,86 (dd, J=11,5 Hz, J=3,2 Hz, 2H, CH<sub>2</sub>O another proton); 4,52 (q, J=7,2 Hz, 2H,  $\frac{\text{CH}_2}{\text{CH}_3}$ ; 4,84 (q, J=11,5 Hz, 4H,ar- $\frac{\text{CH}_2}{\text{C}}$ -O); 7,28–7,66 (m, 10H, ar 1-H, 2-H,  $\overline{\text{7-H}}$ , 8-H, 1'-H, 2'-H, 6'-H, 7'-H, 8'-H); 8,11 (m, 1H, ar 5-H); 8,2–8,26 (m, 2H, ar 4'-H, 5'-H); 8,26–8,28 (m, 1H, ar 4-H). IR (KBr): 3049 (CH ar), 2975, 2931, 2862 (CH alif), 1627, 1599, 1572 (C = C ar), 1238 (C-N), 902 (C-O in oxirane ring). MS(APCI<sup>+</sup>, 20 V), m/z (%): 533([M+H]<sup>+</sup>, 5).

## Results and Discussion

Compounds **4a** and **4b** containing reactive oxiranyl groups were synthesized by the reactions of the corresponding 9-ethyl-3'-hydroxymethyl derivatives **3a** and **3c** with 2-(chloromethyl)oxirane in the presence of KOH as described in Scheme 1. Hydroxymethyl derivatives of **3a**, **3b**, **3c** were obtained by two-step synthesis, which involved formylation of 9-ehyl-3,9'-bicarbazole (**1**) and reduction of the obtained

Scheme 1. The synthesis of compounds 4a and 4b containing reactive oxiranyl groups.

formyl derivatives 2a, 2b and 2c respectively with sodium borohydride. The structures of the synthesized compounds were confirmed by <sup>1</sup>H NMR-, IR- and mass spectrometries.

Reaction conditions a: POCl<sub>3</sub>, DMF; b: NaBH<sub>4</sub>, MeOH; c: 2-(chlormethyl)oxirane, KOH, Na<sub>2</sub>SO<sub>4</sub>.

The UV absorption and fluorescence spectra of dilute THF solutions of compounds 1, 3a, b, c, 4a, b are presented in Fig. 1. For the comparison UV and fluorescence spectra of the dilute solution of 9-ethylcarbazole is given. Low energy absorption maxima of the synthesized materials appear at the wavelengths close to that of 9-ethylcarbazole and close to that of compound 1. Fluorescence spectra of dilute solutions of the derivatives 3–4 are very similar to that of compound 1, which

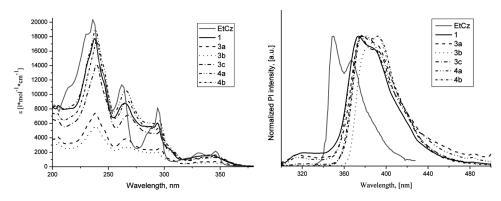


Figure 1. UV absorption and FL emission spectra spectra of compounds 1, 3a, b, c, 4a, b and 9-ethylcarbazole. [The dilute THF solutions  $(10^{-5} \text{ mol } 1^{-1})$ ].

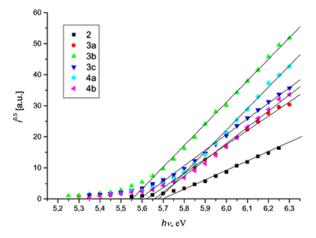


Figure 2. Electron photoemission spectra of the films of compounds 1, 3a, b, c, 4a, b.

possesses rather high triplet energy (2.98 eV) and was successfully applied in blue electrophosphorescent devices [9]. Introduction of epoxypropyl groups into the structures of compounds **4a**, **b** shoud not significantly inluence their photophysical properties and these materials are also expected to posses high triplet energies. The red shift of fluorescence spectra of compounds **1**, **3a**, **b**, **c**, **4a**, **b** relative to that of 9-ethylcarbazole can apparently be explained by a certain intramolecular interation of the chromophores in the excited singlet state.

An important characteristic of electronically active compounds used in optoelectronic devices is ionization potential  $(I_p)$ , which characterizes the electron releasing work under illumination and corresponds to HOMO energy. The ionization potentials  $(I_p)$  of the synthesized compounds were estimated from electron photoemission

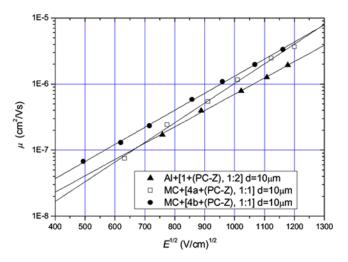


Figure 3. Electric field dependencies of hole drift mobility in charge transport layer of compounds 1, 4a, b doped in PC-Z.

Compound	1	3a	3b	3c	4a	4b
$I_{\rm p}$ , eV	5,70	5,61	5,55	5,58	5,67	5,68

Table 1. The electronic characteristics of compounds 1, 3a, b, c, 4a, b

spectra (Fig. 2), which were recorded in air. The values of  $I_p$  of the synthesized materials are given in Table 1. They are rather close and range from 5.55 to 5.70 eV.

Time-of-flight measurements were used to characterize charge-transporting properties of the synthesized compounds. The electric field dependencies of hole drift mobility for the molecular dispersions of the selected materials in bisphenol Z polycarbonate (PC-Z) are shown in Fig. 2. The solid solutions of 1, 4a, b in PC-Z demonstrated hole drift mobility values in the range from  $2.1 \cdot 10^{-6}$  to  $4.5 \cdot 10^{-6}$  cm<sup>2</sup>/V·s at an electric field of  $1.2 \cdot 10^{6}$  V/cm at the room temperature.

The preliminary examination of photocrosslinking of compound 4b having two oxiranyl groups initiated with diphenyliodonium tetrafluoroborate  $[(C_6H_5)_2I^+BF_4^-]$  (3 mol%/monomer) was carried out at the room temperature. The solution of monomer and photoinitiator in dichloromethane (monomer concentration 25%) was coated onto a silicium glass and dried in vacuum. The process was monitored by IR spectrometry. It was established that absorption band of epoxy groups at 902 cm<sup>-1</sup> fully disappear after 60 minutes of irradiation with a 240 W medium pressure mercury lamp. The photophysical and photoelectrical properties of the cross-linked systems will be reported elsewhere.

In conclusion, we have synthesized new oxiranyl-substituted derivatives of 3,9'-bicarbazole and have studied their optical, photophysical and photoelectrical properties. The electron photoemission spectra of the materials revealed the ionization potentials ranging range from 5.55 to 5.70 eV. Time-of-flight hole drift mobilities of bisphenol Z polycarbonate doped with 50 wt.% exceed  $10^{-6}$  cm<sup>2</sup>/V·s.

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