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ORIGINAL PAPER

Synthesis and properties of 2-(10,11-dihydrodibenz[b,f]azepine-5-yl)carbazole-based monomers and polymers

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Abstract The synthesis of a series of 2-(10,11-dihydrodibenz(b,f)azepinyl)carbazole-based monomers is reported. Full characterization of their structures is presented. The monomers were subjected to cationic polymerization using $BF_3{\cdot}O(C_2H_5)_2$ as an initiator. The synthesized monomers and polymers were examined by differential scanning calorimetry, UV spectrometry, cyclic voltammetry and electron photoemission spectrometry. The electrochemical investigation of the solutions of the synthesized compounds revealed HOMO values ranging from −5.12 to −5.06 eV. Electron photoemission spectrometry of the solid samples gave ionization potentials of 5.40–5.50 eV.

Keywords Carbazole · Iminodibenzyl · Cationic polymerization · Ionization potential

Introduction

Derivatives of carbazole have been widely investigated for their electrical and optical properties [1]. Amongst carbazolyl-containing compounds poly(*N*-vinylcarbazole) was the first to be recognized as a classical hole-transporting material as well as good photoconductor and was extensively exploited in xerographic application [2]. Carbazole derivatives have drawn attention due to their versatility in functionalization, variety of linking topologies, good chemical, environmental stability, etc. Nowadays carbazole-based polymers, oligomers and low-molar-mass compounds are successfully utilized in organic light-emitting diodes (OLEDs), organic solar cells, biosensors, organic-thin-film transistors and other devices [3–9]. There is a

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substantial number of studies devoted to 3,6-substituted carbazole compounds and to their optoelectronic applications [3, 10, 11]. The number of studies on 2- and 2,7-substituted carbazole derivatives increased recently when the efficient preparation route to 2- and 2,7-dihalogenated carbazoles was developed [12–16]. It was shown that 2,7-substituted carbazole derivatives have more extended π-conjugation system than their 3,6-substituted counterparts [16, 17]. Polymers and copolymers having 2,7-disubstituted carbazole units have been attracting much attention as reliable materials for the application in light-emitting diodes, field-effect transistors and photovoltaic cells [1, 18–20]. Amongst these polymers derivatives having 2,7-disubstituted carbazole units in the main chain prevail. Much less attention has been paid to the synthesis and studies of polymers containing 2- or 2,7-disubstituted carbazole units as the side pendants. In our previous study [21], we reported on the synthesis and properties of monomers and polymers incorporating dibenzazepine moieties at the 3rd position of carbazole ring. In this study, we report on the synthesis and properties of monomers and polymers containing 10,11-dihydrodibenz(b,f)azepine moiety at the 2nd position of carbazole ring.

Experimental

Instrumentation

^{1}H and ^{13}C NMR spectra were recordered using Varrian Unity Inova [300 MHz (^{1}H), 75.4 MHz (^{13}C)] apparatus. Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX spectrometer. The spectra of solid compounds were performed in KBr pellets. Mass spectra (MS) were obtained on a Waters ZQ 2000 (Waters, Milford, USA). Elemental analysis was performed with an Exeter Analytical CE-440 Elemental. Melting points (m.p.) were measured using Electrothermal Mel-Temp apparatus. The cyclic voltammetry (CV) measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat–galvanostat. Ultraviolet (UV) absorption spectra were recorded with Spectronic Unicam Genesys 8 spectrometer. Fluorescence (FL) emission spectra were recorded with a Hitachi MPF-4 spectrometer and Shimadzu RF-5301PC. Dilute solutions of the materials in tetrahydrofuran (THF) were used for the UV absorption and FL measurements. Differential scanning calorimetry (DSC) measurements were carried out using Perkin-Elmer Diamond DSC apparatus. Thermogravimetric analysis (TGA) was performed on METTLER TOLEDO TGA/SDTA 851^{e} and Netzsch STA 409 with a data acquisition system 414/1. The DSC and TGA experiments were performed in a nitrogen atmosphere at a heating rate of 10 °C/min. The average molecular weights and the molecular weight distributions were estimated by size exclusion chromatography (SEC) using a system including Waters 515 pump, Waters 410 UV detector (254 nm), precolumn [SDV-Gel (PSS), *L*: 5 cm, *D*: 0.8 cm, particle size: 5 μm and pore size 100 Å] and analytical columns [mixed-C PL-Gel (PL), *L*: 2 × 30 cm; *D*: 0.8 cm and particle size 5 μm]. THF was used as eluent at elution rate of 0.5 mL/min. Calibration was carried out using polystyrene standards. The ionization potential of the films of the synthesized

compounds was measured by the electron photoemission spectrometry in air as described before [22]. The samples for the measurements were prepared by dissolving materials in THF and by coating on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer adhesive layer [23]. The measurement method is, in principle, similar to that described in literature [24].

Materials

10,11-Dihydro-5*H*-dibenz(b,f)azepine (iminodibenzyl), 2-chloroethylvinylether, tris-(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), tri-*tert*-butylphosphine (1 M solution in toluene, $(t\text{-}Bu)_3P$) were purchased from Aldrich and used as received. 3-Bromomethyl-3-methyloxetane were purchased from Chemada. Boron trifluoride diethyl etherate [$BF_3{\cdot}O(C_2H_5)_2$] (Aldrich) was distilled before use (bp 125–126 °C). 4-Bromo-2′-nitrobiphenyl (FW = 278 g/mol, m.p.: 124–126 °C) and 2-bromocarbazole (FW = 246 g/mol, m.p.: 248–250 °C) were prepared by the reported procedures [25, 26]. 3-[10,11-Dihydrodibenz(b,f)azepinyl]-9-[2-(vinyloxy)ethyl]carbazole (**3b**) was prepared by the procedure as described in our previous study [21].

General procedure A for the synthesis of compounds **1a** and **1b**

2-Bromocarbazole (1.7 g, 6.9 mmol), 3-bromomethyl-3-methyloxetane or 2-chloroethylvinylether (10.3 mmol), sodium sulphate (0.5 g, 3.5 mmol), potassium hydroxide (1.16 g, 20.7 mmol) and tetrabutylammonium hydrogen sulphate (0.07 g, 0.2 mmol) were stirred in ethylmethylketone (10 mL) at 60 °C for 3 h. After cooling, the reaction mixture was diluted with ethyl acetate and the organic phase was washed with water. After being dried over anhydrous Na_2SO_4 and filtered, the solvent was removed.

2-Bromo-9-[(3-methyloxetane-3-yl)methyl]carbazole (**1a**). The yield was 2.17 g (95%) brownish resin (FW = 330 g/mol). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 1.36 (s, 3H, C$\underline{H}_3$), 4.15 (d, J = 5.7 Hz, 2H, OC$\underline{H}_2$), 4.40 (d, J = 5.5 Hz, 2H, OC$\underline{H}_2$), 4.55 (s, 2H, NC$\underline{H}_2$), 7.26 (t, J = 7.1 Hz, 1H, Ar), 7.36 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 1H, Ar), 7.50 (t, J = 7.1 Hz, 1H, Ar), 7.65 (d, J = 8.0 Hz, 1H, Ar), 8.00 (s, 1H, Ar), 8.15 (d, J = 8.4 Hz, 1H, Ar), 8.20 (d, J = 7.3 Hz, 1H, Ar). IR (KBr, cm^{-1}): 3055 (C–H, Ar); 2962, 2939, 2875 (C–H); 1591, 1450, 1434 (C–C, Ar); 1327 (C–N); 1128 (C–O–C); 837, 761, 752 (C–H, Ar). MS (APCl$^+$, 20 V, m/z): 331 ([M + H]$^+$, 10%).

2-Bromo-9-[2-(vinyloxy)ethyl]carbazole (**1b**). The crude product was crystallized from methanol. The yield was 1.64 g (75%) of white crystals (FW = 316 g/mol, m.p.: 79–81 °C). ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 4.03–4.21 (m, 4H, CH = C$\underline{H}_2$, OC$\underline{H}_2$), 4.54 (t, J = 5.9 Hz, 2H, NC$\underline{H}_2$), 6.41 (dd, J_1 = 14.6 Hz, J_2 = 6.9 Hz, 1H, O–C$\underline{H}$=), 7.31 (t, J = 8.0 Hz, 1H, Ar), 7.39 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 1H, Ar), 7.46 (t, J = 8.0 Hz, 1H, Ar), 7.52 (d, J = 7.0 Hz, 1H, Ar), 7.64 (s, 1H, Ar), 7.95 (d, J = 8.1 Hz, 1H, Ar), 8.10 (d, J = 8.0 Hz, 1H, Ar). IR (KBr, cm^{-1}): 3048 (C–H, Ar); 2927, 2879 (C–H); 1620, 1591, 1474, 1450 (C–C, Ar); 1322

(C–N); 1057 (C–O–C); 833, 779, 741 (C–H, Ar). MS ($APCl^+$, 20 V, *m/z*): 317 ($[M + H]^+$, 10%).

General procedure B for the synthesis of compounds **2a** and **2b**

The mixture of tris(dibenzylideneacetone)dipalladium (0.09 g, 0.1 mmol) and tri-*tert*-butylphosphine (0.02 g, 0.1 mmol) were dissolved under argon in 5 mL of dry toluene and stirred for 10 min at room temperature (performation of the catalyst). Then the mixture of 10,11-dihydro-5*H*-dibenz(b,f)azepine (0.7 g, 3.6 mmol), derivative of bromocarbazole (2.4 mmol) and potassium *tert*-butoxide (1.4 g, 14.4 mmol) in 10 mL dry toluene were added. The reaction mixture was heated at 90 °C for 12 h. After cooling, the reaction mixture was diluted with ethyl acetate and the organic phase was washed with water and brine. After being dried over anhydrous Na_2SO_4 and filtered, the solvent was removed and residue was purified by column chromatography.

2-[10,11-Dihydrodibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole (**2a**) was prepared according to the general procedure B using 2-bromo-9-[(3-methyloxetane-3-yl)methyl]carbazole (**1a**, 0.79 g, 2.4 mmol). The resulting product was purified by column chromatography using hexane/THF (6/1) as an eluent. The yield was 0.69 g (65%) of brownish resin (FW = 444 g/mol). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 1.25 (s, 3H, C$\underline{H}_3$), 2.94 (s, 4H, C$\underline{H}_2$–C$\underline{H}_2$), 4.04 (d, J = 5.7 Hz, 2H, OC$\underline{H}_2$), 4.21 (d, J = 5.5 Hz, 2H, OC$\underline{H}_2$), 4.40 (s, 2H, NC$\underline{H}_2$), 7.11 (t, J = 7.3 Hz, 1H, Ar), 7.20–7.53 (m, 10H, Ar), 7.65 (d, J = 8.0 Hz, 1H, Ar), 7.82 (d, J = 8.4 Hz, 1H, Ar), 7.90 (d, J = 7.3 Hz, 1H, Ar), 8.19 (d, J = 7.3 Hz, 1H, Ar). ^{13}C NMR spectrum (75.4 MHz, DMSO-d_6, δ, ppm): 23.6 (CH_3), 30.8 ($2CH_2$), 42.7 (CH), 48.6 (NCH_2), 80.2 (OCH_2 in oxetane ring), 106.8, 109.8, 114.7, 119.5, 119.7, 120.9, 123.3, 124.5, 127.9, 130.6, 131.9, 138.8, 141.7, 144.0, 149.1. IR (KBr, cm^{-1}): 3053 (C–H, Ar); 2954, 2925, 2874 (C–H); 1488, 1466, 1456 (C–C, Ar); 1317 (C–N); 1062 (C–O–C); 781, 751 (C–H, Ar). MS ($APCl^+$, 20 V, *m/z*): 445 ($[M + H]^+$, 100%). Elemental analysis. Calcd for $C_{31}H_{28}N_2O$ (%): C 83.75, H 6.35, N 6.30; found (%): C 83.00, H 6.48, N 6.27.

2-[10,11-Dihydrodibenz(b,f)azepinyl]-9-[2-(vinyloxy)ethyl]carbazole (**2b**) was prepared according to the general procedure B using 2-bromo-9-[2-(vinyloxy)ethyl]carbazole (**1b**, 0.76 g, 2.4 mmol). The resulting product was purified by column chromatography using hexane/THF (20/1) as eluent. The yield was 0.65 g (63%) of yellowish powder (FW = 430 g/mol). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 3.09 (s, 4H, C$\underline{H}_2$–C$\underline{H}_2$), 3.97–4.02 (m, 3H, CH=C$\underline{H}_2$, OC$\underline{H}_2$), 4.16 (dd, J_1 = 14.3 Hz, J_2 = 2.6 Hz, 1H, CH=C$\underline{H}_2$), 4.36 (t, J = 5.9 Hz, 2H, NC$\underline{H}_2$), 6.37 (dd, J_1 = 14.3 Hz, J_2 = 7.0 Hz, 1H, O–C$\underline{H}$=), 7.19–7.40 (m, 11H, Ar), 7.56 (d, J = 7.7 Hz, 1H, Ar), 7.80 (d, J = 9.5 Hz, 1H, Ar), 7.95 (d, J = 7.7 Hz, 1H, Ar), 8.20 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR spectrum (75.4 MHz, $CDCl_3$, δ, ppm): 31.1 ($2\underline{C}H_2$), 42.2 (N$\underline{C}H_2$), 65.8 (CH=$\underline{C}H_2$), 87.2 (O$\underline{C}H_2$), 92.55 ($\underline{C}$H=CH$_2$), 107.1, 108.3, 114.9, 119.2, 119.3, 120.9, 123.9, 124.0, 127.4, 130.5, 131.3, 138.7, 140.7, 144.1, 151.5. IR (KBr, cm^{-1}): 3054 (C–H, Ar); 2973, 2931, 2870 (C–H); 1629, 1598 (C=C), 1488, 1462 (C–C, Ar); 1328 (C–N); 1148 (C–O–C); 775, 759, 745 (C–H, Ar). MS ($APCl^+$, 20 V, *m/z*): 431 ($[M + H]^+$,

100%). Elemental analysis. Calcd for $C_{30}H_{26}N_2O$ (%): C 83.69, H 6.09, N 6.51; found (%): C 83.30, H 6.41, N 6.37.

General procedure C for the synthesis of polymers **P1** and **P2**

Monomer with oxetanyl- or vinyloxyethyl group (1.1 mmol) was dissolved in 2 mL of dichloroethane under nitrogen. Then $BF_3{\cdot}O(C_2H_5)_2$ (0.055 mmol, 6.4 μL) was added to the solution and the reaction mixture was stirred for 2 h at 60 °C under argon. After the initiator of reaction was neutralized by ammonia solution. Then the reaction mixture was concentrated by evaporation. The obtained product was isolated by precipitation into methanol.

Poly{2-[10,11-dihydrodibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole} (**P1**) was prepared according to the general procedure C using 2-[dibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole (**2b**, 0.49 g, 1.1 mmol). After Soxhlet extraction (24 h) with methanol and re-precipitation in methanol, the yield of polymer **P1** was 60% (0.29 g). ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.60–1.06 (m, 3H, $C\underline{H}_3$), 2.72–3.05 (m, 4H, $C\underline{H}_2$–$C\underline{H}_2$), 3.10–3.50 (m, 6H, $OC\underline{H}_2$, $OC\underline{H}_2$, $NC\underline{H}_2$), 6.73–8.50 (m, 15H, Ar). IR (KBr, cm^{-1}): 3054 (C–H, Ar); 2962, 2927, 2876 (C–H); 1629, 1598, 1487, 1460 (C–C, Ar); 1328 (C–N); 1101 (C–O–C); 775, 748, 724 (C–H, Ar). SEC (THF, polystyrene standard): $M_n = 2930$, $M_w = 7170$.

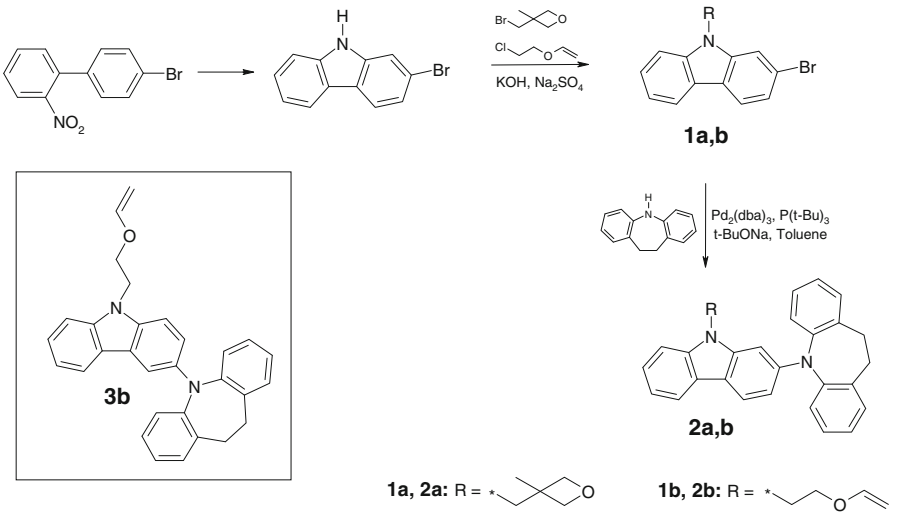
Poly{2-[10,11-dihydrodibenz(b,f)azepinyl]-9-[2-(vinyloxy)ethyl]carbazole} (**P2**) was prepared according to the general procedure C using 2-[10,11-dihydrodibenz(b,f)azepinyl]-9-[2-(vinyloxy)ethyl]carbazole (**2c**, 0.47 g, 1.1 mmol). After Soxhlet extraction (24 h) by methanol and re-precipitation in methanol, the yield of polymer **P2** was 55% (0.26 g). ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 1.51–1.72 (m, 2H, $C\underline{H}_2$), 2.65–3.21 (m, 4H, $C\underline{H}_2$–$C\underline{H}_2$), 3.40–4.57 (m, 5H, OCH_2, NCH_2, $OC\underline{H}$), 6.71–8.00 (m, 15H, Ar). IR (KBr, cm^{-1}): 3022 (C–H, Ar); 2929 (C–H); 1628, 1599, 1488, 1462 (C–C, Ar); 1297 (C–N); 1092 (C–O–C); 801, 775, 747 (C–H, Ar). SEC (THF, polystyrene standard): $M_n = 5530$, $M_w = 10780$.

Results and discussion

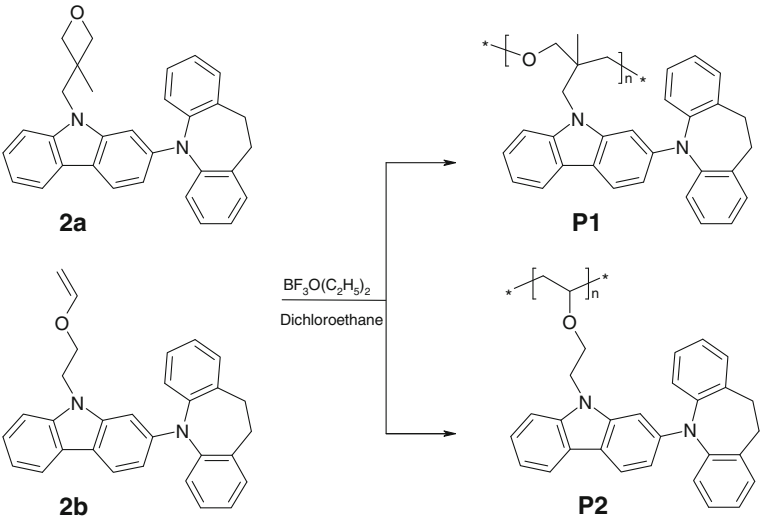
Monomers **2a**, **b** were synthesized by synthetic route comprising the reactions of 2-bromo-9*H*-carbazole with 3-bromomethyl-3-methyloxetane or 2-chloroethylvinylether, followed by a palladium-catalyzed aromatic C–N coupling reactions of 2-bromo-9-alkylcarbazoles with an excess of 10,11-dihydro-5*H*-dibenz(b,f)azepine (Scheme 1).

For the comparison of thermal, optical, electrochemical and photoelectrical properties of 2- and 3-substituted carbazoles, 3-[10,11-dihydrodibenz(b,f)azepinyl]-9-[2-(vinyloxy)ethyl]carbazole (**3b**) was synthesized by the procedure reported in our previous study [21] (Scheme 1).

Oxetanyl- and vinyloxyethyl-functionalized monomers **2a** and **2b** were used for the synthesis of polymers **P1** and **P2** by cationic polymerization (Scheme 2). The monomers were subjected to polymerization in 1,2-dichloroethane solutions using



Scheme 1 Synthesis of monomers **1a**, **b** and **2a**, **b**



Scheme 2 Synthesis of carbazole-based polymers **P1** and **P2**

$BF_3{\cdot}O(C_2H_5)_2$ as an initiator. Low-molecular-weight fractions were removed by Soxhlet extraction with methanol.

The structures of all the compounds were confirmed by ^1H and ^{13}C NMR and IR spectroscopies. In addition low-molar-mass compounds were characterized by mass spectrometry and elemental analysis. The data were found to be in good agreement with the proposed structures. The number average (M_n) and weight average (M_w) molecular weights of the products of polymerization were estimated by SEC using

Table 1 SEC data for polymers **P1** and **P2**

Compound	M_w	M_n	M_w/M_n	DP
P1	7170	2930	2.4	7
P2	10780	5530	1.9	13

Table 2 Thermal characteristics of 2-carbazole derivatives

Compound	**2a**	**2b**	**P1**	**P2**
T_g^a (°C)	5	20	165	184
T_{ID}^b (°C)	335	323	397	363

[a] Determined by DSC with the scan rate of 10 °C/min, N_2 atmosphere

[b] 5% Weight loss temperature determined by TGA with the heating rate of 10 °C/min, N_2 atmosphere

polystyrene standards. The data obtained are summarized in Table 1. The values of weight average degree of polymerization (DP) are presented in Table 1. SEC results indicate that the cationic polymerizations yield polymers of moderate molecular weights with M_w 7170 (for polymer **P1**) and 10780 (for polymer **P2**). The higher molecular weight of **P2** is in agreement with the general behaviour of such monomers, as reported in literature, where a clearly higher reactivity of vinyl ether monomers relative to that of oxetanes is reported [27, 28]. Lower molecular weight, broader molecular weight distribution and lower DP of polymer **P1** can apparently be explained by more intense chain transfer reactions which occur during the cationic polymerization of oxetane monomer **2a** [29].

The behaviour under heating of the monomers and polymers was studied by DSC and TGA under nitrogen atmosphere. The values of glass transition temperatures (T_g) and of 5% weight loss temperatures (T_{ID}) are summarized in Table 2.

All the compounds were obtained as amorphous materials and only glass transitions were observed in their DSC scans and no peaks due to crystallization and melting appeared. Cooling down and following repeated heating revealed only the glass transitions again. However, only polymers **P1** and **P2** formed glasses above the room temperature.

TGA experiments revealed that the thermal stability of 2-substituted carbazole compounds is relatively high and similar to that of the earlier reported 3-substituted counterparts [21]. 2-Substituted carbazole compounds **2a**, **b** and **P1**, **P2** show 5% weight loss temperatures T_{ID} over 300 °C. The polymers exhibit higher T_{ID} than the corresponding monomers (Table 2).

The optical and photophysical properties of dilute solutions of the synthesized compounds were investigated by UV and FL spectrometries. Wavelengths of the lowest energy absorption maxima and FL maxima of monomers **2a**, **b** and polymers **P1**, **P2** are summarized in Table 3. All of these compounds show nearly the same absorption and FL peak wavelengths, due to the presence of the same chromophore. Figure 1a shows UV spectra of monomer **2b** and polymer **P2**. For the comparison the UV spectra of the unsubstituted in the ring carbazole derivative 9-ethylcarbazole (EtCz) is given. UV spectra of compounds **2b** and **P2** are nearly identical with only

Table 3 Absorption and emission characteristics of 2-substituted carbazole derivatives **2a**, **b** and **P1**, **P2**, and 3-substituted carbazole compound **3b**

Compound	UV, λ^{a}_{abs} (nm)	FL, λ^{b}_{fluo} (nm)	Stokes shift (nm)
2a	342	363	21
2b	342	363	21
P1	342	368	26
P2	346	370	24
3b	386	410	24

[a] Wavelengths of lowest energy absorption maxima in solutions (10^{-5} M in THF)

[b] Wavelengths of FL maxima in solutions (10^{-5} in THF, $\lambda_{ex} = 310$ nm)

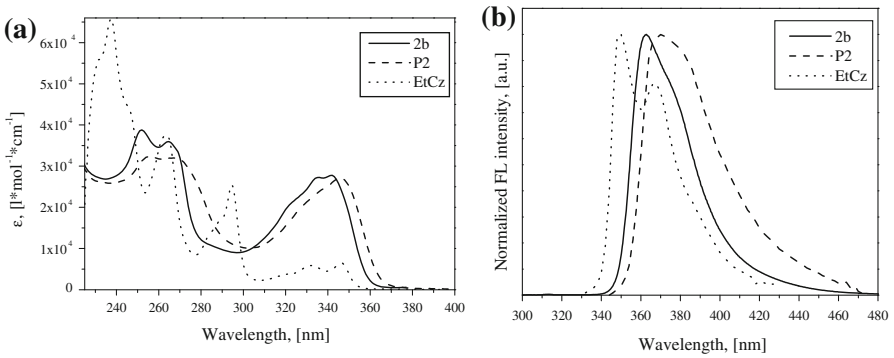


Fig. 1 **a** UV spectra of the dilute THF solutions (10^{-5} M) of monomer **2b**, polymers **P2** and EtCz; **b** the normalized FL spectra of the dilute THF solutions of **2b**, **P2** and EtCz ($\lambda_{ex} = 310$ nm)

of about 4 nm red shift of the spectrum of polymer **P2** relative that of monomer **2b**. However, the spectra of these compounds are totally different from that of EtCz. The absorption of compounds **2b** and **P2** are more intensive between 300 and 370 nm as compared with unsubstituted EtCz.

FL spectra of dilute THF solutions of monomer **2b** and polymer **P2** are shown in Fig. 1b. The intensity was normalized for the comparison of maximum emission wavelengths. FL emission bands of compounds **2b** and **P2** are similar with only 7 nm red shift of the spectrum of polymer. Relatively low Stokes shifts, slightly exceeding 20 nm, are observed for the synthesized materials. Polymers show by 3–5 nm longer Stokes shifts. Apparently, conformations of these materials in the excited state are similar to those of the ground state.

It is of interest to compare optical and photophysical properties of compound **2b** with those of its 3-substituted analogue **3b** reported in our previous study [21]. The absorption and emission characteristics of **3b** are given in Table 3. 3-Substituted carbazole compound **3b** show a significant red shift in absorption (44 nm) and FL (47 nm) with respect to those of 2-substituted analogue **2b**. This observation can apparently be explained by the dependence of electronic communication between carbazole and dibenzazepine moieties on their linking topology. Earlier, we

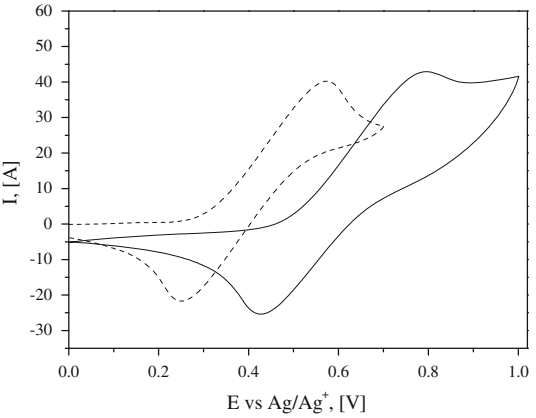


Fig. 2 Cyclic voltammograms of 2-substituted carbazole derivative **2b** (*solid line*) and its 3-substituted analogue **3b** (*dashed line*) measured at scan rate of 50 mVs^{-1} versus Ag/Ag^{+} in a solution of TBAP (0.1 M) in CH_2Cl_2

observed for 2,7-disubstituted carbazole compound up to five times larger radiative relaxation rates, threefold increase in the FL quantum yield and absorbance as well as the reduced electron–vibronic system coupling compared to its 3,6-substituted analogue [30].

The electrochemical stability and the reversibility of the redox process of the synthesized compounds were studied using the CV. The measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) as electrolyte, $Ag/AgNO_3$ as the reference electrode and a Pt wire counter electrode. The experiments were calibrated with the standard ferrocene/ferrocenium redox system [31].

The cyclic voltammograms of monomers **2a**, **b** and polymers **P1**, **P2** show one reversible oxidation couple and no reduction waves. Figure 2 shows CV curve of 2-substituted carbazole monomer **2b**. For the comparison, the CV curve of its 3-substituted analogue **3b** is given. The CV curve of 2-substituted carbazole compound **2b** is shifted positively as compared to the curve of its 3-substituted analogue.

Taking −4.8 eV as the HOMO level for the ferrocene/ferrocenium redox system [31], HOMO energy levels were calculated for the synthesized monomers and polymers. The electrochemical data are summarized in Table 4. The HOMO values of the synthesized compounds are rather close and range from −5.12 to −5.06 eV (Table 4). The LUMO levels were determined from optical energy band gaps $\left(E_g^{op}\right)$ and E_{HOMO} values. Compounds **2a**, **b** and **P1**, **P2** exhibit close LUMO energy levels ranging from −1.82 to −1.60 eV.

The E_{HOMO} values determined by CV do not represent any absolute solid-state or gas-phase ionization energies, but can be used only for the comparison of different compounds. It was therefore of interest to estimate the ionization potentials of the amorphous layers of the synthesized compounds. The ionization potential (I_p) was measured by the electron photoemission in air method, and results are presented in Table 4. Usually, the photoemission experiments are carried out in vacuum, and high vacuum is one of the main requirements for these measurements. If the vacuum

Table 4 HOMO, LUMO, band gap energies and electrochemical characteristics of 2-substituted carbazoles **2a**, **b** and **P1**, **P2**, and 3-substituted carbazole compound **3b**

Compound	$E_{1/2}$ vs. Fc (V)	E_g^{opt} [a] (eV)	I_p^b (eV)	E_{HOMO}^c (eV)	E_{LUMO}^d (eV)
2a	0.30	3.44	5.40	−5.10	−1.66
2b	0.26	3.44	5.42	−5.06	−1.62
P1	0.32	3.43	5.50	−5.12	−1.69
P2	0.27	3.39	5.44	−5.07	−1.68
3b	0.06	3.04	5.34	−4.86	−1.82

[a] The optical band gaps E_g^{opt} estimated from the edges of electronic absorption spectra

[b] Ionization potential was measured by the photoemission in air method from films

[c] $E_{HOMO} = 4.8 + (E_{1/2} - E_{1/2}^{Fc})$, when $E_{1/2}^{Fc} = 0.35$ V

[d] $E_{LUMO} = E_{HOMO} - E_g^{opt}$

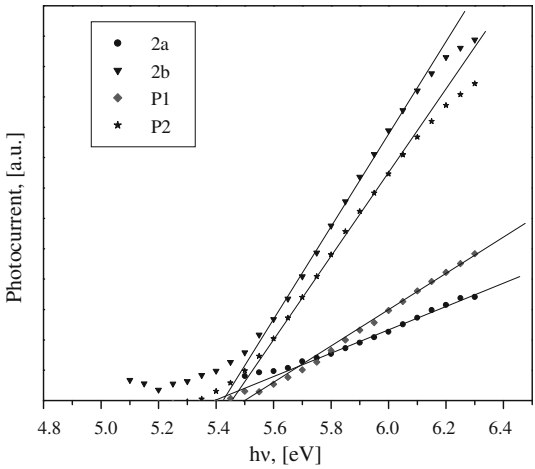


Fig. 3 Electron photoemission spectra of the amorphous films of 2-substituted carbazole compounds **2a**, **b** and **P1**, **P2** measured in air at 25 °C

is not high enough, the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are resistant enough to oxidation and the measurements may be carried out in air. Electron photoemission spectra of the amorphous films of monomers **2a**, **b** and polymers **P1**, **P2** are presented in Fig. 3. The ionization potentials of the synthesized compounds vary in the range from 5.40 to 5.50 eV. The I_p values for the films of 2-substituted carbazole compounds are higher than that of 3-substituted analogues [21]. This observation is consistent with the results of electrochemical measurements. 2-Substituted derivatives **2a**, **b** and **P1**, **P2** exhibit lower HOMO energy levels than 3-substituted derivative **3b**. Nevertheless, with ionization potentials of 5.40–5.50 eV these materials can potentially be applied in optoelectronic devices, such as electrophotographic photoreceptors and light-emitting diodes. I_p values for charge generation materials, including those widely used in electrophotographic photoreceptors pigments, are in the range of 5.1–5.6 eV [32–35]. I_p of the materials

synthesized are also close to that of indium-tin oxide ($\sim$4.9 eV), which is used as an anode in various optoelectronic devices [36].

Conclusions

We have synthesized low-molar-mass 2-substituted carbazole-based compounds and polymers. Polymerization of oxetane and vinyl ether compounds with cationic initiator $BF_3{\cdot}O(C_2H_5)_2$ yielded polymers with number-average molecular weights of 2930 and 5530. The polymers exhibit sufficient thermal stability and form amorphous films with glass transition temperatures of 165 and 184 °C. The optical properties of synthesized monomers and polymers are very similar due to the presence of the same chromophore. In electrochemical measurements the synthesized 2-substituted carbazole compounds behave similarly. They are electrochemically stable, the oxidation of the synthesized compounds is reversible. The values of ionization energy of amorphous films of the synthesized derivatives range from 5.40–5.50 eV.

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