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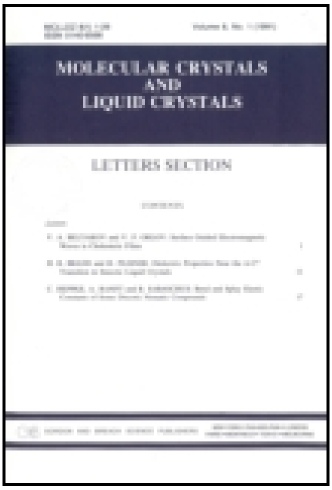

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Synthesis and Properties of Triindole-Based Monomers and Polymers

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Synthesis and Properties of Triindole-Based Monomers and Polymers

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New star-shaped derivatives of 10,15-dihydro-5H-diindolo[3,2-a:3′,2′-c]carbazole (triindole) with reactive functional groups are synthesized. Triindole monomers were found to have similar profiles of absorption and fluorescence spectra due to the presence of the same chromophore. The ionization potentials of the monomers are found to be comparable (5.37–5.53 eV). Hole drift mobilities of the amorphous layers of oxetane and vinyl ether molecularly dispersed in bisphenol Z polycarbonate (50%) exceed 10^{-5} cm^2/Vs at high electric fields. Cationic photocross-linking of triindole containing oxirane, oxetane and vinyl ether initiated with diphenyliodoniun tetrafluorborate is carried out.

Keywords Triindole; photo-crosslinking; ionization potential; hole mobility

Introduction

Charge-transporting materials play a key role in organic light-emitting diodes, as well as in other electronic and optoelectronic devices, such as organic and hybrid photovoltaic devices, and organic thin film transistors [1,2,3]. Organic molecules containing in their structure electron-rich chromophores such as carbazole and indolocarbazole have been known as good hole-transporting materials [4,5,6,7]. Carbazolyl groups have long been recognized in the construction of charge-transporting amorphous materials [8]. Carbazolyl groups can be included into the different structures including the peripheral lateral chains of discotic cores [8]. 10,15-Dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (triindole) can be treated as an overlapping framework of three carbazole units [9]. The investigation of properties of triindole derivatives such as 5,10,15-trimethyl-10,15-dihydro-5H-diindolo[3,2-a:3′,2′-c]carbazole (N-trimethyltriindole) has shown that this chromophore is an attractive unit for the synthesis of hole transporting materials due to its high hole drift mobility [10].

In this article, we report on the synthesis and the characterization of new 10,15-dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (triindole)-based hole-transporting glass-forming materials containing reactive functional groups. The presence of reactive functional groups in

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these structures makes them useful for the preparation of the cross-linked charge transporting materials. Cross-linkable electroactive materials are useful for the preparation of the multilayer devices by spin coating. Cross-linking can also be used for the improvement of the morphological stability of the active layers of optoelectronic devices.

Experimental

Instrumentation

IR spectra were recorded using a Specord 75 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Unity Inova [300 MHz (^{1}H), 75.4 MHz (^{13}C)] spectrometer at room temperature. All the data are given as chemical shifts δ (ppm) downfield from $Si(CH_3)_4$. Mass spectra were obtained on a Waters Micromass ZQ mass spectrometer. UV spectra of $2\cdot10^{-5}$ M solutions of the synthesized monomers in THF were recorded on a Perkin Elmer Lambda 35 spectrometer using a microcell with an internal width of 1 mm. Steady state fluorescence spectra were recorded with a Hitachi MPF-4 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out in the nitrogen atmosphere with a TA Instruments Q10 calorimeter at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on Mettler TGA/SDTA851e/LF/1100 in the nitrogen atmosphere at a heating rate of 20°C/min. 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. The measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) as an electrolyte, Ag/AgNO3 as the reference electrode, and a Pt wire as a counter electrode. The experiments were calibrated with the standard ferrocene/ferrocenium redox system. Ionization potentials ($I_{p(ep)}$) of the films of the synthesized compounds were measured by the method of electron photoemission in air as described before [11]. Hole drift mobilities were measured by the xerographic time-of-flight (XTOF) method [12,13,14]. The electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of a nitrogen laser (pulse duration was 1 ns, wavelength 337 nm). The capacitance probe that was connected to the wide frequency band electrometer measured the speed of the surface potential decrease (dU/dt).

Materials

Diphenyl iodonium tetrafluoroborate (TB) was synthesized and purified as described before [15]. 3-Bromomethyl-3-methyloxetane was purchased from Chemada Fine Chemicals and used without further purification. Ammonium thiocyanate, cyanuric chloride, benzyltrimethylammoniumchloride (BTMA), potassium hydroxide, sodium sulfate, sodium hydride, epichlorohydrin, 2-chlorethylvinylether, *p*-vinylbenzylchloride were purchased from Aldrich and used as received. 10,15-dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (triindole) (**1**) was synthesized by the procedure described earlier [16].

*5,10,15-tris(oxyran-2-ylmethyl)-10,15-dihydro-5H-diindolo[3,2-a:3′,2′-c]carbazole (**2a**).* 10,15-dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (**1**) (1 g, 2.9 mmol) and 2-(chloromethyl)oxirane (2.68 g (29 mmol) were dissolved in 60 ml of ethylmethylketone. Then KOH (1.46 g, 26.1 mmol) and Na_2SO_4 (0,62 g, 4,35 mmol) were added into the solution. The reaction mixture was stirred for 24 h at a temperature of 40ºC. After the completion of the reaction (TLC control, eluent hexane/acetone 3:1), the reaction mixture was filtrated. The product was purified by silica gel column chromatography using hexane/acetone (4:1) as an eluent. It was recrystallized from the eluent mixture of solvents. The yield of compound **2a** was 0.45 g (30%). M.p.: 248–250°C. ^{1}H NMR (DMSO, 300 MHz) δ, ppm.: 2.63–2.70 (m, 3H, 3 × 1H of CHO); 2.87 (m, 3H, 3 × 1H of CHO); 3.50–3.59 (m, 3H, 3 × 1H of CHO); 4.91–5.02 (m, 3H, 3 × 1H of CHN); 5.31–5.44 (m, 3H, 3 × 1H of CHN); 7.40 (t, 3H, $J = 7.1$ Hz, Ar); 7.50 (t, 3H, $J = 7.3$ Hz, Ar); 7.93 (d, 3H, $J = 8.0$ Hz, Ar); 8.39 (d, 3H, $J = 7.9$ Hz, Ar). ^{13}C NMR (DMSO, 75 MHz) δ, ppm.: 45.55; 48.55; 51.68; 103.62; 112.40; 121.24; 122.25; 122.97; 124.19; 139.17; 142.24. IR (KBr), ν, (cm^{-1}): 3050 (C—H, Ar); 2992, 2918 (C—H, Alif); 1579 (C=C, Ar); 1472 (C—H, Alif.); 1297 (C—N); 1212, 950, 845 (C—O—C); 747, 729 (C—H, Ar). MS(APCI$^+$, 20 V), m/z (%): 514 ([M + H]$^+$, 100).

*5,10,15-tris((3-methyloxetan-3-yl)methyl)-10,15-dihydro-5H-diindolo[3,2-a:3′,2′-c]carbazole (**2b**).* 10,15-Dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (**1**) (1 g, 2.90 mmol) and 3-(bromomethyl)-3-methyloxetane (4.75 g, 26.12 mmol) were dissolved in 60 ml of ethylmethylketone. Then KOH (2.92 g, 52.14 mmol), Na_2SO_4 (1.23 g, 8.66 mmol) and BTMA (0.05 g) were added. The reaction mixture was stirred at 55°C for 23 h. After the completion of the reaction (TLC control, eluent hexane/acetone 3:1), the reaction mixture was filtrated. The product was purified by silica gel column chromatography using hexane/acetone (4:1) as an eluent. It was recrystallized from the eluent mixture of solvents. The yield of compound **2b** was 0.28 g (16%). M.p.: 277–278°C. ^{1}H NMR (DMSO, 300 MHz) δ, ppm.: 0.91 (s, 9H, CH_3); 3.86 (d, 6H, $J = 6.0$ Hz, CH_2O); 4.51 (d, 6H, $J = 5.9$ Hz, CH_2O); 5.23 (s, 6H, CH_2N); 7.40 (t, 3H, $J = 7.2$ Hz, Ar); 7.47 (t, 3H, $J = 7.6$ Hz, Ar); 7.89 (d, 3H, $J = 8.1$ Hz, Ar); 8.12 (d, 3H, $J = 7.7$ Hz, Ar). ^{13}C NMR (DMSO, 75 MHz) δ, ppm.: 22.71; 43.35; 51.58; 80.07; 104.04; 112.61; 121.08; 122.44; 122.92; 123.89; 139.27; 142.12. IR (KBr), ν, (cm^{-1}): 3048 (C—H, Ar); 2956, 2872 (C—H, Alif); 1583, 1556 (C=C, Ar); 1470 (C—H, Alif.); 1281 (C—N); 1225 (C—CH_3); 1240, 1115, 978 (C—O—C); 750, 728 (C—H, Ar). MS(APCI$^+$, 20 V), m/z (%): 598 ([M + H]$^+$, 100).

*5,10,15-tris(2-(vinyloxy)ethyl)-10,15-dihydro-5H-diindolo[3,2-a:3′,2′-c]carbazole (**2c**).* 10,15-Dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (**1**) (1 g, 2.90 mmol) and 2-chlorethylvinylether (1.3 g, 12.20 mmol) were dissolved in 50 ml of acetone. Then KOH (2.92 g, 52.14 mmol), Na_2SO_4 (1.23 g, 8.66 mmol) and BTMA (0.05 g) were added. The reaction mixture was stirred at 55°C for 5 days. After the completion of the reaction (TLC control, eluent hexane/ethylacetate 3:1), the reaction mixture was filtrated. The product was purified by silica gel column chromatography using hexane/ethylacetate (7:1) as an eluent. It was recrystallized from the eluent mixture of solvents. The yield of compound **2c** was 0.23 g (14%). M.p.: 135–137°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ, ppm.: 3.97 (dd, 3H, $J_1 = 6.8$ Hz, $J_2 = 2.4$ Hz, 3 × 1H of $C\underline{H}_2CH$); 4.10 (dd, 3H, $J_1 = 14.3$ Hz, $J_2 = 1.2$ Hz, 3 × 1H of $C\underline{H}_2CH$); 4.17 (t, 6H, $J = 6.9$ Hz, CH_2O);5.32 (t, 6H, $J = 6.9$ Hz, CH_2N); 6.40 (dd, 3H, $J_1 = 14.3$ Hz, $J_2 = 6.8$ Hz,$C\underline{H}CH_2$); 7.38-7.44 (m, 3H, Ar); 7.48-7.55 (m, 3H, Ar); 7.77 (d, 3H, $J = 8.1$ Hz, Ar); 8.27 (d, 3H, $J = 7.7$ Hz, Ar). IR (KBr), ν, (cm^{-1}): 3048 (C—H, Ar); 2923, 2880 (C—H, Alif); 1719 (C—O—C); 1621 (C=C, Alif.); 1563 (C—C, Ar); 1473 (C—H, Alif); 1296 (C—N); 1198 (C—O—C); 825 (C=C, Alif.); 744, 726 (C—H, Ar). MS(APCI$^+$, 20 V), m/z (%): 556 ([M + H]$^+$, 20).

5,10,15-tris(4-vinylbenzyl)-10,15-dihydro-5H-diindolo[3,2-a:3′,2′-c]carbazole **(2d)**. 10,15-Dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (0,5 g, 1.45 mmol) (**1**) and *p*-vinylbenzylchloride (1.99 g, 13.05 mmol) were dissolved in 50 ml of THF. Then NaH (0.36 g, 15 mmol) and BTMA (0.05 g) were added. The reaction mixture was stirred at 50°C for 48 h. After the completion of the reaction (TLC control, eluent hexane/ethylacetate 4:1), the reaction mixture was filtrated. The product was purified by silica gel column chromatography using hexane/ethylacetate (6:1) as an eluent. The yield of compound **2c** was 0.13 g (13%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ, ppm.: 5.32 (dd, 3H, $J_1 = 10.90$ Hz, $J_2 = 0.89$ Hz, $C\underline{H_2}CH$); 5.83 (dd, 3H, $J_1 = 17.62$ Hz, $J_2 = 0.89$ Hz, $C\underline{H_2}CH$); 6.11 (s, 6H, CH_2N); 6.80 (dd, 3H, $J_1 = 17.62$ Hz, $J_2 = 10.91$ Hz, $C\underline{H}CH_2$); 7.04–7.11 (m, 3H, Ar); 7.26–7.30 (m, 6H, Ar); 7.52 (s, 12 H, Ar); 8.04 (d, 3H, $J = 8.08$ Hz, Ar). IR (KBr), ν, (cm^{-1}): 3050 (C—H, Ar); 2979 (C—H, Alif); 1628 (C = C, Alif); 1568 (C—C, Ar.); 1471 (C—H, Alif.); 1297 (C—N); 907 (C=C, Alif); 750, 730 (C—H, Ar). MS(APCI$^+$, 20 V), m/z (%): 694 ($[M + H]^+$, 20).

General Procedure of Photocross-linking

Photopolymerization of monomers (**2a–c**) was carried out in the air atmosphere in the form of thin films (thickness of 20–30 μm). For the preparation of thin films, the solution of a monomer and the diphenyl iodonium tetrafluoroborate (TB) initiator in chloroform was poured on a glass plate and dried in vacuum. The initial concentration of a monomer was 2 wt%, and that of the initiator was 6 mol%/monomer. The polymers were extracted with boiling chloroform for 48 hours.

Poly{5,10,15-tris(oxyran-2-ylmethyl)-10,15-dihydro-5H-diindolo[3,2-a:3′,2′-c]carbazole} (**3a**) was obtained as an amorphous substance. The yield was 5.1%.IR (KBr), ν, (cm^{-1}): 3366 (OH); 3054 (C—H, Ar); 2950 (C—H, Alif); 1609 (C=C, Ar); 1467 (C—H, Alif.); 1329 (C—N); 1084 (C—O—C); 749 (C—H, Ar).

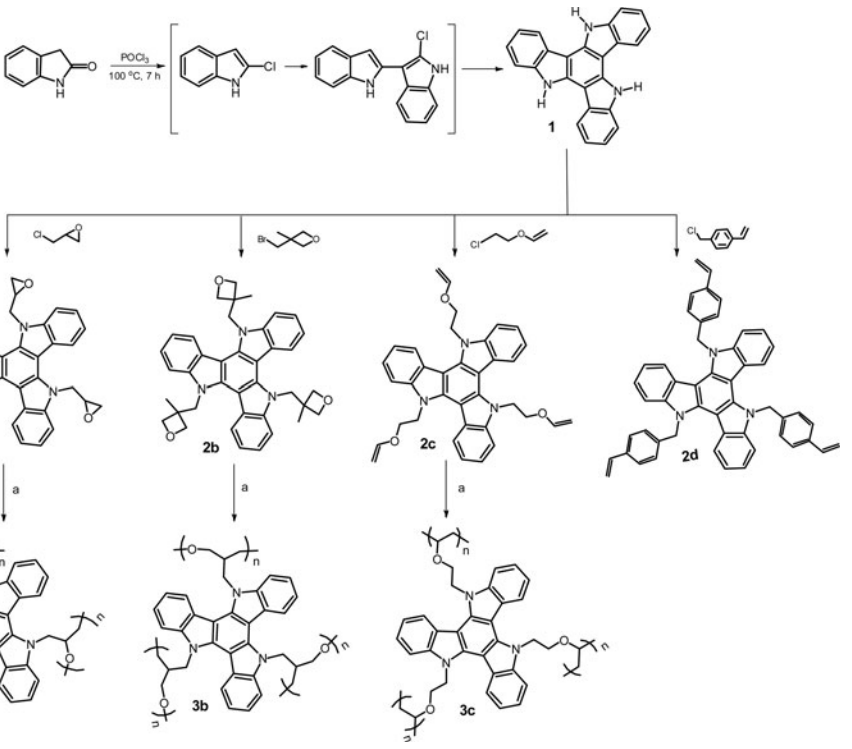
Poly{5,10,15-tris((3-methyloxetan-3-yl)methyl)-10,15-dihydro-5H-diindolo[3,2-a:3′, 2′-c]carbazole} (**3b**) was obtained as an amorphous substance. The yield was 4.4%. IR (KBr), ν, (cm^{-1}): 3421 (OH); 3050 (C—H, Ar); 2961, 2874 (C—H, Alif); 1581 (C=C, Ar); 1467 (C—H, Alif.); 1296 (C—N); 1229 ($C—CH_3$); 980 (C—O—C); 750, 732 (C—H, Ar).

Poly{5,10,15-tris(2-(vinyloxy)ethyl)-10,15-dihydro-5H-diindolo[3,2-a:3′,2′-c]carbazole} **(3c)** was obtained as an amorphous substance. The yield was 62.9%. IR (KBr), ν, (cm^{-1}): 3371 (OH); 3048 (C—H, Ar); 2926, 2875 (C—H, Alif); 1565 (C—C, Ar); 1470 (C—H, Alif); 1294 (C—N); 1051 (C—O—C); 747, 729 (C—H, Ar).

Results and Discussion

The monomers with oxiranyl, oxetanyl, vinyloxyethyl and vinylbenzyl functionalities (**2a–d**) were prepared by synthetic route shown in Scheme 1. All the monomers were synthesized from 10,15-dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (**1**). 10,15-Dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole (triindole) was synthesized by the reaction of oxindole and phosphorus oxychloride using the earlier reported procedure [16]. Monomer **2a** was synthesized from triindole and 2-(chloromethyl)oxirane in the presence of KOH. Monomers **2b–d** were prepared by the reaction of triindole with the excess of 3-(bromomethyl)-3-methyloxethane, (chlorethyl)vinylether, or p-vinylbenzylchloride under basic conditions in the presence of a phase transfer catalyst.

The main advantage of compounds **2a–2d** in comparison with the other derivatives of triindole reported in the literature is their ability to form insoluble cross-linked layers.



Scheme 1. Molecular structures and synthesis pathways for the studied materials.

Photocross-linking of **2a–c** was demonstrated using cationic photoinitiator diphenyl iodonium tetrafluoroborate in the form of thin films. Low-molar-mass fractions of the products of photopolymerization were removed by the Soxleth extraction of the raw polymers with boiling chloroform. The polymeric products were identified by IR spectroscopy. Monomers **2a–d** were also characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and mass spectrometry.

The kinetics of photocross-linking of the monomers with oxetanyl and vinylether functionalities (**2b–c**) initiated with TB was studied by IR spectrometry, as described earlier [17]. Figure 1 shows the conversion of the functional groups versus time curves. The kinetics of photopolymerization of the monomers (**2b**, **2c**) was studied. Upon the UV exposure, the decrease of the intensity of IR absorption bands characteristic of the corresponding oxetanyl and vinyl groups at 978 cm^{-1} and 1621 cm^{-1}, respectively, was recorded. The degree of conversion of the reactive groups at any time during the UV irradiation was established by measuring the peak height under the specific absorption band according to the equation

$$\text{degree of conversion (\%)} = ((A_o - A)/A_o) \times 100,$$

where A_o and A are the absorbency levels of the reactive groups in the photopolymerizable film before and after the UV irradiation during a certain period of time, respectively.

Photocross-linking of the monomers exhibited a relatively high initial rate. After 5 min of irradiation, the degree of conversion of oxetanyl groups of ca. 53% was observed for the photopolymerizations of monomer **2b** and 58% conversion of vinyl groups for the photocross-linking of monomer **2c.** After 90 min of irradiation, 62% conversion of reactive

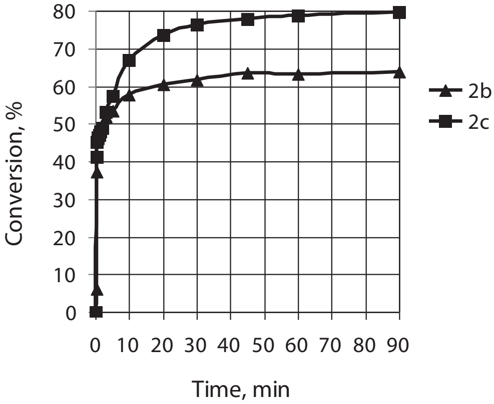


Figure 1. Conversion of reactive functional groups versus time curves for photocross-linking of monomers **2b, 2c** initiated with TB (6 mol%/monomer).

functional groups were observed for oxetane monomer (**2b**) and 80% for vinylether (**2c**). Thus, vinylether **2c** showed a higher initial rate of cross-linking and a higher conversion of the functional groups, as well as the highest yield of cross-linked polymer (62.9%). The yields of cross-linked polymers **3a**, **3b** were rather similar (5.1% and 4.4%) and much lower than that of polymer **3c**.

Due to the presence of the same chromophore, UV and fluorescence spectra of dilute THF solutions of synthesized monomers (**2a–d**) are similar. The UV and fluorescence spectra of dilute THF solutions of compound **2b** are given in Fig. 2. Characteristic maxima at 218, 256, 317 nm are observed in the UV spectrum. These maxima are typical of

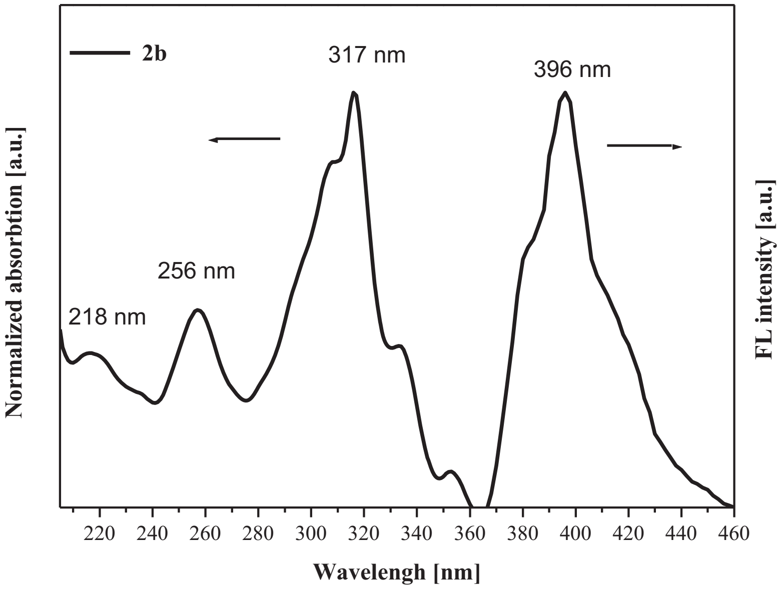


Figure 2. UV and FL ($\lambda_{ex} = 310$ nm) spectra of dilute solution of compound **2b** in THF ($2{\cdot}10^{-5}$ mol/l).

Table 1. Thermal and electrochemical properties of compounds **2a–d**

Compound	T_g, °C	T_m, °C	T_{cr}, °C	T_{ID}, °C	$E_{1/2\ \mathrm{vs\ Fc}}$,[d] [V]	EA,[e] [eV]	$I_{p(cv)}$,[f] [eV]	$I_{p(ep)}$,[g] [eV]
2a	—	255[a,]	232	393	0.40	—1.78	5.20	5.37
2b	116[b]	285[a]	—	413	0.43	—1.81	5.23	5.53
2c	—	131[a], 138[a,b]	106	381	0.34	—1.72	5.14	5.43
2d	146[b]	—	—	453	0.38	—1.76	5.18	5.47

DSC thermograms of compounds (scan rate 10°C/min, N_2 atmosphere) [a] 1st heating; [b] 2nd heating; [c]. $E_{1/2\ \mathrm{vs\ Fc}} = E_{1/2} - E_{Fc}$; $E_{1/2} = 1/2(E_{pc} + E_{pa})$ oxidation potentials were obtained as the average value between each anodic and corresponding cathodic potential, $E_{Fc} = 0.23$ V vs. $Ag/AgNO_3$. [e] $I_{p(cv)} = E_{1/2\ \mathrm{vs\ Fc}} + 4.8$ eV .[f] EA = – ($I_{p(cv)}$ – E_{opt}). [g] Ionization energy was measured by the method of photoemission in air from films.

alkyltriindole [18]. The estimated optical band gap (E_{opt}) is the same for all the synthesized compounds and is equal to 3.42 eV. The profiles of fluorescence spectra of monomers were found to be invariant with respect to the excitation wavelength and similar.

The thermal properties of the monomers were examined by TGA and DSC. The thermal characteristics are summarized in Table 1. The onsets of the thermal degradation (T_{ID}) of the monomers range from 381 to 453°C. Monomers **2a–c** were obtained as crystalline materials. Monomer **2a** cannot be transformed into the glassy state by cooling from the melt, whereas monomer **2b** formed glasses upon cooling from the melt. Its glass transition reached 116°C. The molecular glass of **2b** seems to be morphologicaly stable. The sample of this compound did not crystallize when heated above the glass transition temperature. Monomer 2c showed the polymorphism in the first heating scan with the melting points of 131 and 138°C. It can be transformed into the glassy state. However, we were not able to estimate its glass transition temperature. Compound **2d** was isolated after the synthesis as an amorphous substance. Its glass transition was observed at 146°C.

To elucidate the energetic conditions for energy and electron transfers in dilute solutions, the synthesized compounds were studied by cyclic voltammetry (CV). The CV measurements were carried out using a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as an electrolyte and $Ag/AgNO_3$ as a reference electrode. Each measurement was calibrated with ferrocene (Fc). The electrochemical data are summarized in Table 1. The cyclic voltammograms of **2a**–**d** show a quasireversible oxidation couple and no reduction waves. The oxidation potentials for the reversible oxidation were taken as the average of the anodic and cathodic peak potentials. The ionization potentials ($I_{p(cv)}$) and the electron affinities (EA) were also estimated by using the empirical formulas $I_{p(cv)} = E_{1/2\mathrm{vsFc}} + 4.8$ eV and EA = –($I_{p(cv)}$ – E_{opt}) [19]. Electron photoemission method was used for the determination of $I_{p(ep)}$ values for thin films of **2a–d**, and the results are presented in Table 1. The $I_{p(ep)}$ values were found to be comparable due to the presence of the same chromophore (5.37-5.53 eV). The value of $I_{p(cv)}$ estimated for **2a–d** is close to a value of $I_{p(ep)}$ directly measured by the electron photoemission method.

Xerographic time-of-flight (XTOF) measurements were used to characterize the charge transport properties of the selected compounds (**2b, c**). The XTOF curves of the solid solution of **2c** in bisphenol Z polycarbonate (PC-Z) are presented in Fig. 3. After the

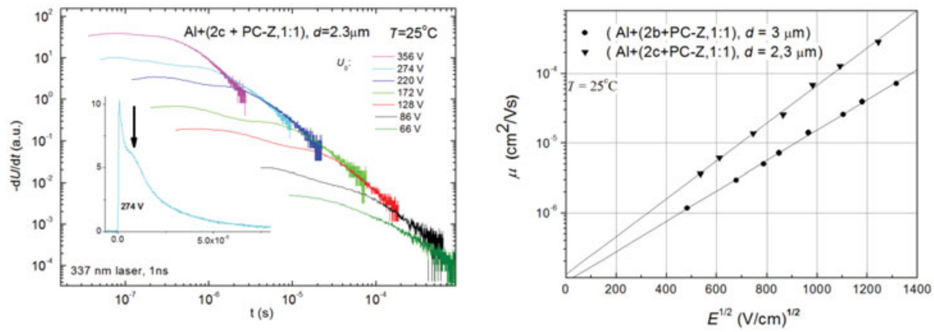


Figure 3. (**a**) XTOF transients of **2c** doped in PC-Z (50%), insert shows one of the transient curves in linear plot, the arrow marks transit time. (**b**) Electric field dependencies of hole drift mobility in the layers of molecular dispersion of compounds **2b** or **2c** in PC-Z (50%).

photoexcitation of the sample with a short light impulse, the rate of potential discharge in the XTOF measurements has a plateau region. The kink noted with the arrow at the end of the plateau respects the transit time of the fastest carriers in the sample, and the time was used to calculate the hole drift mobility.

Electric field dependences of the hole drift mobility (μ_h) in the layers of **2b-c** are presented in Fig. 3. The charge drift mobilities show the linear dependences on the square root of the electric field. The μ_h values of the molecular dispersion layers of compounds **2b** or **2c** in bisphenol Z polycarbonate (PC-Z; 50%) are 5.6×10^{-6} and 1.9×10^{-5}, respectively, at electric field of 6.4×10^5 V cm^{-1}. The higher charge mobilities by at least one order of magnitude could be predicted for the films of the pure compounds. The values of hole drift mobility for compounds **2a**, **2d** were not measured due to their recrystalization from the solid state solutions in PC-Z.

Conclusions

We have synthesized 10,15-dihydro-5*H*-diindolo[3,2-a:3′,2′-c]carbazole-based monomers, containing oxiranyl, oxetanyl, vinyloxyethy, and vinyl benzyl reactive functional groups. Cationic photocross-linking in the solid state of the monomers with oxiranyl, oxetanyl, and vinyloxyethyl groups initiated with diphenyliodoniun tetrafluorborate was carried out. Optical, photophysical, electrochemical, and thermal properties of the synthesized compounds were studied. The dilute solutions of the synthesized derivatives exhibit the absorption in the range 210–360 nm, and fluorescence in the range 370–460 nm. The spectra of the compounds have the similar profiles due to the presence of the same chromophore. Monomers show a high thermal resistance, and their 5% mass loss temperatures are higher than 381°C. Monomers with vinyloxyethyl, vinyl benzyl, and oxetanyl functionalities are capable to form glasses. The ionization potentials are independent of functional groups and are in the range of experimental errors (5.37–5.53 eV). The synthesized compounds are capable of charge transporting. Hole drift mobilities of the amorphous layers of compounds having oxetanyl and vinyl ether functionalities and molecularly dispersed in bisphenol Z polycarbonate (50%) exceed 10^{-5} cm^2/Vs at high electric fields.

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