

New derivatives of indazole as electronically active materials

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ABSTRACT

Synthesis and thermal, optical, electrochemical and photoelectrical properties of new indazole-based electroactive materials are reported. 1-Phenyl-5(6)-[*N,N*-(bisphenyl)]aminoindazoles and their methoxy-substituted analogues exhibit high thermal stabilities with the onset temperatures of thermal degradation ranging from 352 to 424 °C. The synthesized indazole derivatives form glasses with glass transition temperatures ranging from 35 to 39 °C. The synthesized compounds are electrochemically stable: their cyclic voltammograms show one reversible oxidation couple and no reduction waves. The ionization potentials of the solid samples of the synthesized materials are in the range of 5.3–5.9 eV. Methoxy-substituted derivatives show lower ionization potentials. Time-of-flight hole drift mobilities of 50% solid solution of 1-(4-methoxyphenyl)-5-[*N,N*-(bis(4-methoxyphenyl))]aminoindazole in bisphenol Z polycarbonate reach 10^{-5} cm²/V s at high electric fields.

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1. Introduction

Different classes of organic electronically active materials are nowadays widely studied and used as the components of optoelectronic and electronic devices such as solar cells, organic light-emitting diodes, organic thin-film transistors [1–3]. Arylaldehyde hydrazones are widely studied and used as charge-transporting materials mainly in electrophotographic photoreceptors of copying and fax machines as well as of laser printers [4]. Hydrazones can be also of interest as unimolecular half-substractors for molecular processors [5]. The main advantages of hydrazones are their simple synthesis and capability of effectively transporting positive charges, i.e., holes. Among hole-transporting hydrazones arylamine and carbazole-based compounds prevail [6–10]. Among cyclic analogues of hydrazones only 1,3,5-triaryl-2-pyrazolines have attracted attention of researchers as charge-transporting materials [11,12]. Hole mobility in a single crystal of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline was almost independent on the applied electric field, and was found to be about 10^{-2} cm² V⁻¹ s⁻¹. In the glassy state the hole mobility dropped to 10^{-5} cm² V⁻¹ s⁻¹. Indazole derivatives are widely studied and used as biologically active materials [13,14]. To our knowledge indazoles have not yet

been explored as charge-transporting materials. The aim of this work was design and synthesis of new derivatives of indazole as charge-transporting materials with potential application in organic optoelectronics.

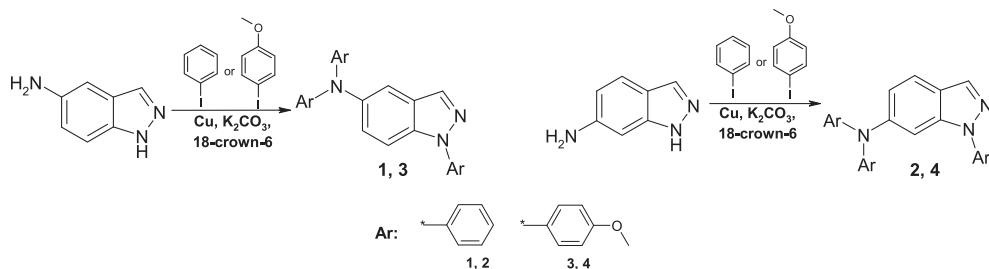
2. Experimental

2.1. Instrumentation

¹H NMR and ¹³C NMR spectra were recorded using Varian Unity Inova [300 MHz (¹H), 75.4 MHz (¹³C])] spectrometer. All the data are given as chemical shifts *d* (ppm) downfield from Si(CH₃)₄. IR spectra were recorded using Perkin Elmer 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^{-5} M solutions of the synthesized compounds in tetrahydrofuran (THF) were recorded on Perkin Elmer Lambda 35 spectrometer using a microcell with an internal width of 1 mm. Steady state fluorescence spectra were recorded with Hitachi MPF-4 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out in a 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 a nitrogen atmosphere at a heating rate of 20 °C/min. Melting points were measured on Electrothermal MEL-TEMP melting point apparatus. The ionization potentials (*I*_p) of the films of the synthesized compounds were

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Scheme 1.

measured by electron photoemission in air as described before [15]. The samples for ionization potential measurements were prepared as described previously [16]. Hole drift mobilities were measured by a xerographic time-of-flight (XTOF) method [17–19]. The samples for the charge carrier mobility measurements were prepared by procedure as we described earlier [20]. The thickness of the charge-transporting layers was 6–7 mm.

2.2. Materials

5-Aminoindazole, 6-aminoindazole, iodobenzene, 4-iodoanisole, potassium carbonate, 18-crown-6, copper powder were purchased from Aldrich and used as received.

2.3. General procedure A

Compounds **1–4** were prepared by Ullmann coupling [21]. The reaction mixtures consisting of 5- or 6-aminoindazole (7.51 mmol), potassium carbonate (135.18 mmol), the corresponding aryl iodide (41.31 mmol), copper powder (75.10 mmol), 18-crown-6 (3.76 mmol) and 1,2-dichlorobenzene (ca. 10 ml) were stirred at the reflux temperature for 48 h. The reactions were monitored by thin-layer chromatography (TLC). The reaction mixtures were cooled down and filtrated. Then the solvent was distilled in vacuum and the crude product was subjected to silica gel column chromatography.

1-phenyl-5-[N,N-(bisphenyl)]aminoindazole (1). The mixture of ethyl acetate and hexane in volume ratio of 1:4 was used as an eluent for column chromatography. The yield of pink amorphous powder was 7% (0.2 g).

MS (APCI⁺, 20 V), *m/z* (%): 362 ([M + H]⁺, 100).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.00–7.14 (m, 6H, Ar), 7.24–7.42 (m, 7H, Ar), 7.52–7.60 (m, 2H, Ar), 7.71 (d, 1H, *J* = 9.00 Hz, Ar), 7.73–7.78 (m, 2H, Ar), 8.09 (d, 1H, *J* = 0.88 Hz, Ar).

IR. ν_{max} (KBr): (C–H Ar) 3034, (C=C Ar) 1597, 1588, 1491, (C–N) 1272.

1-phenyl-6-[N,N-(bisphenyl)]aminoindazole (2). The mixture of ethyl acetate and hexane in volume ratio of 1:4 was used as an eluent for column chromatography. Yellowish crystals were obtained after recrystallization from the eluent mixture of solvents with the yield of 11% (0.3 g). Mp = 164–166 °C.

MS (APCI⁺, 20 V), *m/z* (%): 362 ([M + H]⁺, 100).

¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm): 6.92 (dd, 1H, *J*₁ = 1.85 Hz, *J*₂ = 6.84 Hz, Ar), 7.05–7.11 (m, 6H, Ar), 7.25 (s, 1H, Ar), 7.29–7.37 (m, 5H, Ar), 7.48–7.54 (m, 2H, Ar), 7.57–7.62 (m, 2H, Ar), 7.79 (dd, 1H, *J*₁ = 0.60 Hz, *J*₂ = 8.09 Hz, Ar), 8.29 (d, 1H, *J* = 0.95 Hz, Ar).

IR. ν_{max} (KBr): (C–H Ar) 3032, (C=C Ar) 1623, 1589, 1494, 1469, (C–N) 1290, 1276.

1-(4-methoxyphenyl)-5-[N,N-[bis(4-methoxyphenyl)]aminoindazole (3). The mixture of THF and hexane in volume ratio of 1:4

was used as an eluent for column chromatography. The yield of yellow resin was 14% (0.47 g).

MS (APCI⁺, 20 V), *m/z* (%): 452 ([M + H]⁺, 45).

¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm): 3.83 (s, 6H, –OCH₃), 3.91 (s, 3H, –OCH₃), 6.82–6.87 (m, 4H, Ar), 7.02–7.11 (m, 6H, Ar), 7.20–7.25 (m, 1H, Ar), 7.33 (s, 1H, Ar), 7.53 (d, 1H, *J* = 9.11 Hz, Ar), 7.61–7.65 (m, 2H, Ar), 8.01 (s, 1H, Ar).

IR. ν_{max} (KBr): (C–H) 2929, (–O–CH₃) 2833, (C=C Ar) 1502, 1462, (C–O–C) 1239.

1-(4-methoxyphenyl)-6-[N,N-[bis(4-methoxyphenyl)]aminoindazole (4). The mixture of ethyl acetate and hexane in volume ratio of 1:4 was used as an eluent for column chromatography. Brown crystals were obtained after recrystallization from methanol with the yield of 7% (0.21 g). Mp = 112 and 133 °C (DSC).

MS (APCI⁺, 20 V), *m/z* (%): 452 ([M + H]⁺, 70).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.83 (s, 6H, –OCH₃), 3.87 (s, 3H, –OCH₃), 6.83–6.88 (m, 4H, Ar), 6.89–6.93 (m, 1H, Ar), 6.96–7.02 (m, 2H, Ar), 7.07–7.11 (m, 5H, Ar), 7.47–7.53 (m, 2H, Ar), 7.56–7.59 (m, 1H, Ar), 8.06 (d, 1H, *J* = 0.88 Hz, Ar).

IR. ν_{max} (KBr): (C–H) 2951, 2930, 2833, (–O–CH₃) 2833, (C=C Ar) 1621, 1506, 1475, 1465, (C–O–C) 1241.

3. Results and discussion

Arylaminosubstituted derivatives of N aryl indazole (**1–4**) were synthesized as described in Scheme 1 by Ullmann coupling of 5- or 6-aminoindazole with the corresponding iodoaryl derivatives. Compounds **1–4** were purified by column chromatography. They were identified by elemental analysis: IR-, ¹H NMR and mass spectrometries.

The behaviour under heating of the synthesized compounds was studied by DSC and TGA under a nitrogen atmosphere. The values of glass transition temperatures (*T*_g), melting points (*T*_m), crystallization temperatures (*T*_{cr}) and the temperatures of the onsets of thermal degradation (*T*_{ID}) are summarized in Table 1. The newly synthesized compounds demonstrate high thermal stability. The temperatures of the onset of thermal degradation range from 352 to 424 °C, as established by TGA with a heating rate of 20 °C/min. *T*_{ID} of compounds **1–4** is considerably higher than that earlier observed for carbazolyl hydrazones [22]. Indazole derivatives **1** and **3** having aromatic amino group at the 5-th position of indazole moiety show higher thermal stability than the corresponding derivatives **2** and **4** having the substituents at the 6-th

Table 1
Thermal characteristics of compounds **1–4**.

Compound	<i>T</i> _m °C	<i>T</i> _{cr} °C	<i>T</i> _g °C	<i>T</i> _{ID} °C
1	—	—	36	396
2	169	131	35	352
3	—	—	36	424
4	112, 133	—	39	415

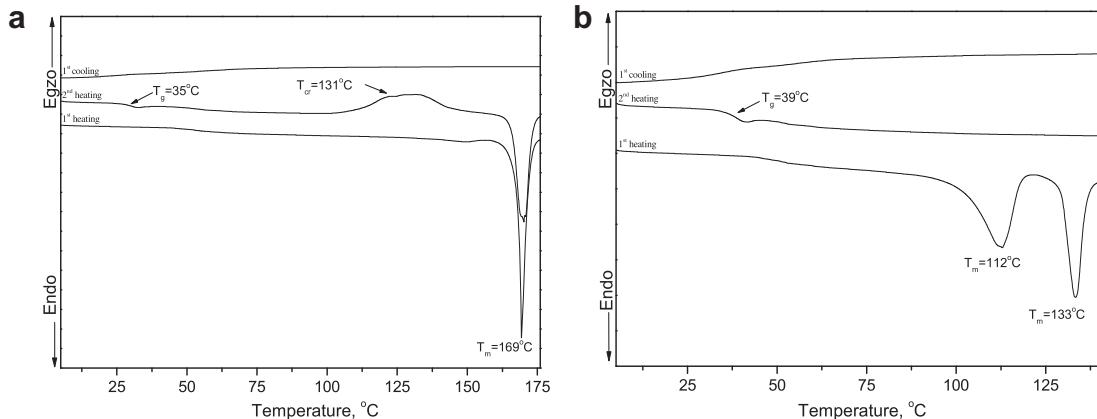


Fig. 1. DSC thermograms of compounds 2 (a), 4 (b) (scan rate of $10^\circ\text{C}/\text{min}$. N_2 atmosphere).

position. Introduction of methoxy groups at the 4-th position of phenyl rings leads to the increase of the thermal stability. Compounds **3** and **4** show higher T_{ID} than compounds **1** and **2**.

Compounds **1** and **3** were isolated after the synthesis as amorphous substances. When their samples were heated glass-transitions were observed at 36°C and no peaks due to crystallization and melting appeared. Cooling down and the following repeated heating revealed only glass transition. Compounds **2** and **4** were isolated after the synthesis as crystalline materials. In the first DSC heating scans they showed endothermic melting signals with the melting points in the range of 112 – 169°C . These compounds formed glasses upon cooling from the melts. In the second heating scans they showed glass-transitions at 35°C and 39°C respectively. For the illustration of the above stated DSC curves of compounds **2**, **4** are shown in Fig. 1. The morphological stability of the molecular glass of **2** seems to be somewhat lower than that of the other compounds reported in this work. In the second DSC heating scan it shows not only glass transition at 35°C but also crystallization at 131°C and melting at 169°C . Compound **4** showed polymorphism. In the first DSC heating scan it revealed two endothermal melting signals at 112 and 133°C . The ability of a solid material to exist in more than one form or crystal structure was earlier observed for other organic glass-forming electroactive materials [23,24].

The UV absorption and fluorescence spectra of dilute solutions of compounds **1**–**4** in THF are shown in Fig. 2. Compounds **1**–**4** exhibit broad absorption up to 400 nm with λ_{max} in the range of 237 – 362 nm . Indazole derivatives **1** and **3** having aromatic amino group at the 5-th position of indazole moiety exhibit red shifted

absorption edge relative to the corresponding 6-substituted isomers (**2** and **4**). Introduction of methoxy substituents into phenyl groups leads to further red shift of absorption spectra. The absorption edges of compounds **3** and **4** show bathochromic shifts with respect of absorption edges of compounds **1** and **2**.

In the region of 260 – 320 nm two peaks are observed in the UV spectra of compounds **2**, **4** compounds UV spectra 260 – 320 nm region, however in the spectra of **1**, **3** only one broad peak is observed. Calculations with semi-empirical methods (AM1 for geometrical optimization and ZINDO/S for excitation energy with CI from 2 occupied and 2 unoccupied MO) show that peaks of $\pi \rightarrow \pi^*$ transitions at ca. 260 nm for compounds **2**, **4** can belong to transitions in $\text{HOMO} \rightarrow \text{LUMO} + 1$ and $\text{HOMO-1} \rightarrow \text{LUMO}$ orbitals. LUMO orbitals for all four compounds are located on electron-accepting benzimidazole moiety. For compounds **2**, **4** HOMO-1 orbitals are located on phenylbenzimidazole moiety and do not reach one phenyl ring of diphenylamino moiety. For compounds **1**, **3** HOMO-1 orbitals are more delocalized and located on whole molecules. This can cause red shift of $\text{HOMO-1} \rightarrow \text{LUMO}$ transition peak in the spectra of **1**, **3** which leads to overlapping by intensive absorption band of $\text{HOMO} \rightarrow \text{LUMO}$ transition with the maximum at ca. 300 nm . As a result in UV spectra of **1**, **3** one broad peak in 260 – 320 nm region is observed, contrary to spectra of **2**, **4** which have two peaks in the same region.

Fluorescence maxima of the derivatives **1**–**4** appear in the region of wavelengths from 401 to 441 nm . Introduction of methoxy substituents into phenyl groups of 1-phenyl-5(6)-[*N,N*-(bisphenyl)]aminoindazole leads to the red shift of fluorescence

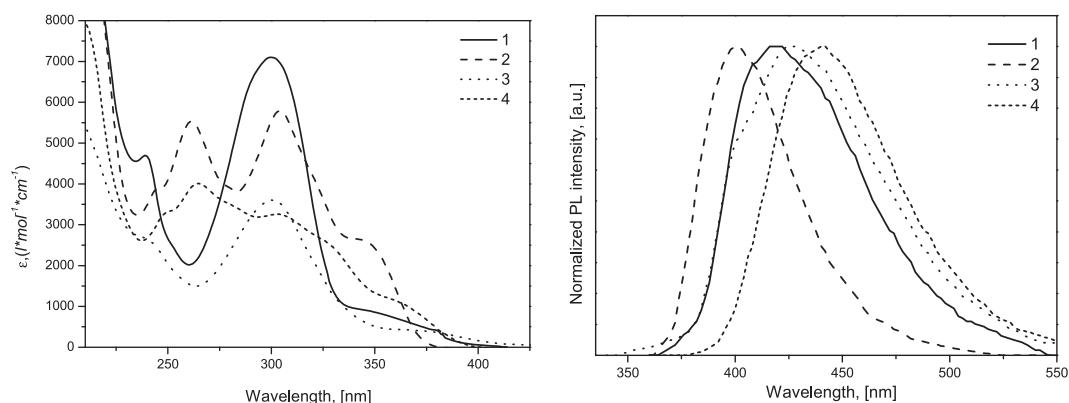


Fig. 2. UV absorption and fluorescence spectra of dilute THF solutions ($10^{-4}\text{ mol l}^{-1}$) of compounds **1**–**4**.

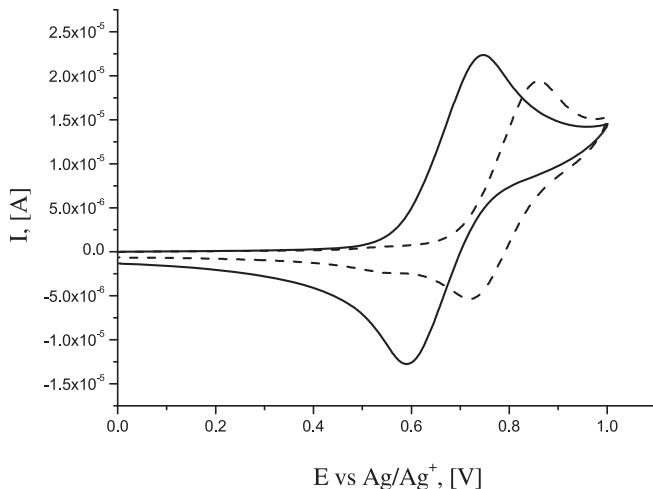


Fig. 3. Cyclic voltammograms of 10^{-4} M solutions of **1** (solid line) and **2** (dashed line) measured at a scan rate of 50 mV s^{-1} vs Ag/Ag^+ in a solution of TBAP (0.1 M) in CH_2Cl_2 .

emission maxima. Fluorescence spectra of the dilute solutions compounds **3** and **4** exhibit bathochromic shifts with respect of the spectra of compounds **1** and **2**. This observation is consistent with the UV spectrometry data.

The electrochemical stability and the reversibility of the redox process of the synthesized compounds were studied by cyclic voltammetry (CV). The measurements of 10^{-4} M solutions of the synthesized compounds were carried out with a glassy carbon electrode (diameter 2 mm) in dichloromethane solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) as electrolyte, Ag/AgNO_3 as the reference electrode (electrolyte solution of 0.01 M AgNO_3 and of 0.1 M TBAP in acetonitrile) and a Pt wire counter electrode. The experiments were calibrated with the standard ferrocene/ferrocenium redox system [25]. The synthesized compounds were found to be electrochemically stable. Their cyclic voltammograms show one quasi-reversible oxidation couple and no reduction waves. **Fig. 3** shows CV curves of 5- and 6-substituted indazole compounds **1** and **2** respectively. The CV curve of 6-substituted indazole compound (**2**) is shifted positively as compared to that of its 5-substituted analogue (**1**).

Taking -4.8 eV as the HOMO level for the ferrocene/ferrocenium redox system, HOMO energy levels were calculated for the synthesized compounds. The electrochemical data are summarized in **Table 3**. The HOMO values of the synthesized compounds range from -5.31 to -4.92 eV . The HOMO energy levels of 6-substituted indazole compounds (**2**, **4**) are lower than those of the corresponding 5-substituted analogues (**1**, **3**) (**Table 2**). The LUMO levels were determined from optical energy band gaps (E_g^{opt}) and E_{HOMO}

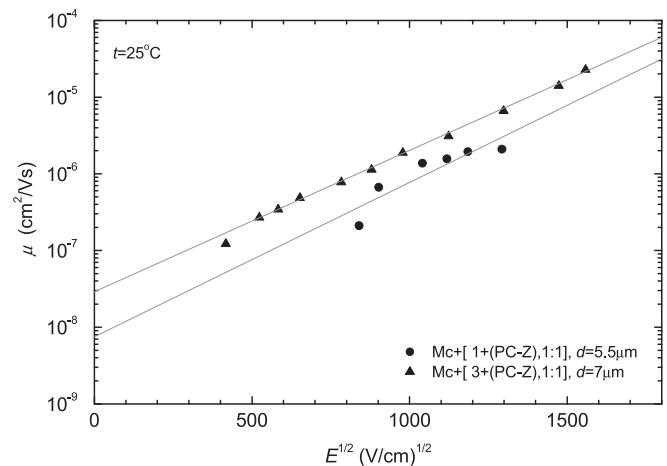


Fig. 4. Electric field dependencies of hole drift mobility for compounds **1** and **3** doped in PC-Z (50%).

values. Compounds **1**–**4** exhibit close LUMO energy levels ranging from -2.05 to -1.80 eV .

An important characteristic of electronically active compounds used in optoelectronic devices is ionization potential (I_p) which characterizes the electron releasing work under illumination. The ionization potentials (I_p) of the solid samples of **1**–**4** were measured by electron photoemission technique in air. The values of I_p are presented in **Table 2**. The ionization potentials of the synthesized materials range from 5.3 to 5.9 eV . The ionization potentials of compounds **3** and **4** having methoxy phenyl groups are lower than those of compounds **1** and **2**. This observation confirms our earlier observation that introduction of methoxy groups into the structures of aromatic amines enables to decrease their ionization potentials [26]. The ionization potentials of 5-substituted indazole compounds **1** and **3** are a little lower than those of their corresponding 6-substituted analogues (**2** and **4**). This observation correlates with UV absorption spectrometry and cyclic voltammetry data.

Compounds **1** and **3** showing the best solubility and compatibility with bisphenol Z polycarbonate (PC-Z) were used for the estimation of charge transport properties by xerographic time-of-flight technique. **Fig. 4** shows electric field dependencies of hole drift mobilities (μ) in the films of bisphenol Z polycarbonate molecularly doped with compounds **1** and **3**. At the room temperature μ shows linear dependencies on the square root of the electric field. The hole drift mobility values are summarized in **Table 3**. The solid solutions of **1** and **3** in PC-Z demonstrated hole drift mobility values of 3×10^{-7} and $8.3 \times 10^{-7} \text{ cm}^2/\text{V}\cdot\text{s}$ respectively at electric fields of $6.4 \times 10^5 \text{ V/cm}$. Thus introduction of methoxy groups into *para* positions of phenyl moieties enables not only to decrease ionization potentials but also to improve charge transport properties. At high electric field hole drift mobilities of compound **3** doped in PC-Z (50 wt.%) reach $10^{-5} \text{ cm}^2/\text{V}\cdot\text{s}$. These are rather high charge mobilities keeping in mind that charge mobilities in pure amorphous molecular materials are usually by 1–2 order of magnitude higher than those observed in molecularly doped polymers.

Table 2
HOMO, LUMO, band gap energies and electrochemical characteristics of compounds **1**–**4**.

Compound	$E_{1/2}$ vs Fc, [V] ^b	E_g^{opt} , [eV] ^a	E_{I} , [eV] ^b	E_{HOMO} , [eV] ^c	E_{LUMO} , [eV] ^d
1	0.38	3.15	5.6	-5.18	-2.03
2	0.51	3.26	5.9	-5.31	-2.05
3	0.12	2.95	5.3	-4.92	-1.97
4	0.14	3.14	5.4	-4.94	-1.80

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

^b Ionization energy was measured by the photoemission in air method from films.

^c $E_{\text{HOMO}} = 4.8 + (E_{1/2} - E_{1/2}^{\text{Fc}})$, when $E_{1/2}^{\text{Fc}} = 0.28 \text{ V}$.

^d $E_{\text{LUMO}} = E_{\text{HOMO}} - E_g^{opt}$.

Table 3
Hole mobility data for the molecular mixtures of compounds **1** and **3** with PC-Z.

Transport material + host polymer	d , [μm]	μ_0 , [cm^2/Vs] ^a	μ , [cm^2/Vs] ^a
1 + (PC-Z), 1:1	5.5	7.5×10^{-9}	3×10^{-7}
3 + (PC-Z), 1:1	7	3×10^{-8}	8.3×10^{-7}

^a Hole drift mobility values at electric field $6.4 \times 10^5 \text{ V/cm}$.

In conclusion, we have synthesized and characterized new indazole-based electroactive materials and studied their thermal, optical, photophysical and photoelectrical properties. The synthesized indazole derivatives were found to constitute glass-forming materials with glass transition temperatures in the range of 35–39 °C as characterized by differential scanning calorimetry. Electron photoemission spectra of the amorphous films of the materials revealed ionization potentials of 5.3–5.9 eV. Time-of-flight hole drift mobilities of 50% solid solution of 1-(4-methoxyphenyl)-5-{N,N-[bis(4-methoxyphenyl)]}aminoindazole (**3**) in bisphenol Z polycarbonate reach 10^{-5} cm²/V·s at high electric fields.

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