

Polymeric and low-molar-mass glass-forming diphenylsulphone-based hydrazones

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New polymeric hydrazones were prepared by polycondensation of bis(4-hydrazinophenyl)sulfone with the differently substituted diformyl carbazoles. Their optical, thermal and photoelectrical properties were studied and compared with those of the new and earlier synthesized low-molar-mass glass-forming diphenylsulfone dihydrazones. The glass transition temperatures of the studied compounds range from 22 to 123°C. The ionisation potentials of the films of diphenylsulfone hydrazone compounds measured by the electron photoemission technique range from 5.00 to 5.88 eV. Hole-drift mobilities in the amorphous films of the solid solutions of one diphenylsulfone dihydrazone in bisphenol Z polycarbonate exceed 10^{-5} cm²/(Vs) at high applied electric fields as characterized by the time-of-flight method.

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1. Introduction

Organic semiconducting polymers and low-molar-mass compounds have attracted much scientific and technological interest during the past few decades because of their applications in electrophotographic photoreceptors [1,2], organic light emitting diodes [3,4] and the potential application in solar cells [5], field effect transistors [6,7] and other optoelectronic and electronic devices.

Hydrazone derivatives are known as effective p-type organic semiconductors [11]. Together with polymer hosts they are used in many commercial electrophotographic photoreceptors [12]. Most of the known aromatic hole-transporting hydrazones are crystalline compounds and they can crystallize in molecularly doped polymers so decreasing the service time of electrophotographic photoreceptors. The use of amorphous aromatic hydrazones would enable to obtain morphologically stable charge-transporting molecularly doped polymers. It would also allow to increase their concentration in the mixtures with polymer hosts and thus to increase charge carrier mobilities in the charge transport layers of electrophotographic photoreceptors.

Herewith we report on the synthesis of new polymeric hydrazones and low-molar mass glass forming compound. We also present the results of investigation of the influence of the different chromophores on the optical and thermal properties of the newly and earlier synthesized glass forming diphenylsulphone dihydrazones. The photoelectric properties are also reported.

2. Experimental

Instrumentation

¹H NMR spectra were recorded with a Bruker AC 250 (250 Hz) and Varian Unity Inova (300Hz) spectrometers.

All data are given as chemical shifts δ (ppm) downfield from (CH₃)₄Si. IR-spectroscopy measurements were performed on a Perkin Elmer Spectrum GX spectrophotometer, using KBr pellets. UV/VIS spectra were recorded with Spectronic Genesys-8 spectrophotometer. Mass spectra were obtained on a Waters Micromass ZQ mass spectrometer. The average molecular weight and the molecular weight distribution were estimated by gel permeation chromatography (GPC) using Waters GPC system including a Waters 410 UV detector and polystyrene standards. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PC Lux and Mettler Toledo TGA/SDTA 851^c apparatus at a heating rate of 10 K/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Pyris Diamond DSC apparatus at a 10 K/min heating rate under nitrogen atmosphere. The samples for ionisation potential and hole-drift mobility measurements were prepared as described previously [13]. The ionisation potentials were measured by the electron photoemission in air method [14]. Hole-drift mobilities were measured by a xerographic time-of-flight method [15].

Materials

Poly((9-ethylcarbazole-3,6-diyl)methylenehydrazino (diphenylsulfone-4,4'-diyl)hydrazinomethylene) (**1a**). A solution of 0.5 g (1.79 mmol) of bis(4-hydrazinophenyl)sulfone (SH) in THF was added dropwise to a solution of 0.5 g (1.99 mmol) of 9-ethylcarbazole-3,6-dicarbaldehyde in THF by stirring. The reaction mixture was stirred at 40 °C for 24 h. Then the reaction mixture was cooled to the room temperature and concentrated. The crude product was precipitated into methanol and filtered. Polymer **1a** was purified by

repeated precipitation into methanol, then filtered and dried in vacuum. Yield 0.9 g (77.6%) of **1a**. IR (in KBr) ν/cm^{-1} : 3288 (N-H), 3055 (ar. C-H), 2974, 2872 (alk. C-H), 1680 (C=N), 1592, 1490 (ar. C=C), 1102 (SO₂). ¹H NMR (DMSO): δ (ppm) : 1.38 (s, 3H, CH₃), 4.28-4.6 (s, 4H, CH₂+NH), 7.22 (d, 2H, $J=7.07$ Hz, CHar.), 7.61 (d, 2H, CHar.), 7.78 (d, 4H, $J=10.3$ Hz, CHar.), 7.86-7.96 (m, 4H, CHar.+CH=N), 8.18 (s, 2H, CHar.), 8.45 (s, 2H, CHar.).

Poly((9-(2-ethylhexyl)carbazole-3,6-diyl)methylenehydrazino(diphenyl sulfone-4,4'-diyl)hydrazinomethylene) (**1b**) was synthesized by the similar procedure as compound **1a**, but 9-(2-ethylhexyl)carbazole-3,6-dicarbaldehyde was used instead of 9-ethylcarbazole-3,6-dicarbaldehyde. Yield 0.8 g (81%) of **1b**. IR (in KBr) ν/cm^{-1} : 3287 (N-H), 3058 (ar. C-H), 2956, 2927, 2870 (alk. C-H), 1678 (C=N), 1592, 1490 (ar. C=C), 1103 (SO₂). ¹H NMR (DMSO): δ (ppm) : 0.69-0.93 (m, 6H, CH₃), 1.09-1.41 (m, 8H, CH₂), 2.01 (s, 1H, CHalk.), 4.08-4.20 (m, 4H, CH₂+NH), 7.22 (d, 2H, $J=8.97$ Hz, CHar.), 7.56-7.67 (m, 2H, CHar.), 7.8 (d, 4H, $J=7.74$ Hz, CHar.), 7.92 (d, 4H, $J=6.98$ Hz, CHar.+CH=N), 8.16 (s, 2H, CHar.), 8.48 (s, 2H, CHar.).

Poly((9-ethylcarbazole-3,6-diyl)methylene-1-butylhydrazino(diphenylsulfone-4,4'-diyl)-1-butylhydrazinomethylene) (**2a**). 0.28 g (0.60 mmol) of polymer **1a** was dissolved in 30 ml of THF. Then 0.25 g (1.37 mmol) of 1-iodobutane and 0.0056 g (0.017 mmol) of phase-transfer catalyst tetrabutylammonium hydrogen sulphate were added. The reaction mixture was heated to 40 °C. Then 0.046 g (0.83 mmol) of powdered potassium hydroxide was added stepwise and the reaction mixture was stirred for 24 h. Then the reaction mixture was cooled to the room temperature and the solvent was evaporated. The crude product was dissolved in chloroform. The inorganic salts were extracted out with water. The chloroform extract was dried with anhydrous sodium sulphate and concentrated. The product was precipitated in methanol, filtered, washed with ethylacetate and dried in vacuum. Yield 0.3 g (65%) of **2a**. IR (in KBr) ν/cm^{-1} : 3064 (ar. C-H), 2958, 2932, 2871 (alk. C-H), 1588, 1491 (ar. C=C), 1116 (SO₂). ¹H NMR (CDCl₃): δ (ppm) : 0.86-0.93 (m, 9H, CH₃), 1.27-1.34 (m, 8H, CH₂), 3.75-3.84 (m, 6H, CH₂), 7.28-7.62 (m, 6H, CHar.), 7.72-8.2 (m, 10H, CHar.+CH=N).

Poly((9-(2-ethylhexyl)carbazole-3,6-diyl)methylene-1-butylhydrazine(diphenyl sulfone-4,4'-diyl)-1-butylhydrazinomethylene) (**2b**) was synthesized by the similar procedure as compound **2a**, but polymer **1b** was used instead of polymer **1a**. The product was precipitated in diethylether, filtered, washed with ethylacetate and dried in vacuum. Yield 0.7 g (74.8%) of **1b**. IR (in KBr) ν/cm^{-1} : 3045 (ar. C-H), 2956, 2928, 2870 (alk. C-H), 1586, 1498 (ar. C=C), 1098 (SO₂). ¹H NMR (CDCl₃): δ (ppm) : 0.83-0.98 (m, 12H, CH₃), 1.01-1.12 (m, 4H, CH₂), 1.2-1.45 (m, 8H, CH₂), 1.69 (s, 4H, CH₂), 2.09 (s, 1H, CHalk.), 3.98 (s, 2H, CH₂), 4.1-4.3 (m, 4H, CH₂), 7.29-7.58 (m, 6H, CHar.), 7.82-8.11 (m, 8H, CHar.+CH=N), 8.36 (s, 2H, CHar.).

Low molecular weight compounds **5a** and **5b** were synthesized by the similar procedure as compounds **3a**, **3b** and **4a**, **4b** [16], but 1-[4-(trifluoromethyl)phenyl]-1H-

pyrrole-2-carbaldehyde was used as a starting formyl derivative.

Di(4-((1-(1-trifluoromethylphenyl-4)pyrrole)-2-methylene-1-butylhydrazino) phenyl)sulphone (**5a**). IR (in KBr) ν/cm^{-1} : 3109, 3079 (ar. C-H), 2951, 2933, 2873 (alk. C-H), 1584, 1497 (ar. C=C), 1324 (C-F), 1097 (SO₂). ¹H NMR (CDCl₃): δ (ppm) : 0.98 (t, 6H, CH₃), 1.35-1.42 (m, 4H, CH₂), 1.5-1.62 (m, 4H, CH₂), 3.78 (t, 4H, CH₂), 6.41 (t, 4H, CHar.), 6.72 (d, 4H, CHar.), 6.91 (q, 2H, CHar.), 7.48-7.6 (m, 6H, CHar. + CH=N), 7.65 (d, 4H, $J=8.83$ Hz, CHar.), 7.79 (d, 4H, $J=7.76$ Hz, CHar.). MS (45 eV): $m/z = 833(\text{M}^+)$, 526, 239.

Di(4-((1-(1-trifluoromethylphenyl-4)pyrrole)-2-methylene-1-hexylhydrazino) phenyl)sulphone (**5b**). IR (in KBr) ν/cm^{-1} : 3119, 3079 (ar. C-H), 2956, 2929, 2856 (alk. C-H), 1586, 1497 (ar. C=C), 1324 (C-F), 1099, (SO₂). ¹H NMR (CDCl₃): δ (ppm) : 0.92 (t, 6H, CH₃), 1.28-1.45 (m, 12H, CH₂), 1.5-1.68 (m, 4H, CH₂), 3.75 (t, 4H, CH₂), 6.44 (q, 2H, CHar.), 6.7-6.8 (m, 6H, CHar.), 6.92 (q, 2H, CHar.), 7.48-7.6 (m, 6H, CHar. + CH=N), 7.68 (d, 4H, $J=9.15$ Hz, CHar.), 7.79 (d, 4H, $J=9.15$ Hz, CHar.). MS (45 eV): $m/z = 889(\text{M}^+)$, 653.

3. Results and discussion

New electroactive polymers **2a** and **2b** were prepared by polycondensation of bis(4-hydrazinophenyl)sulphone with the differently substituted diformyl carbazoles, as shown in Fig. 1.

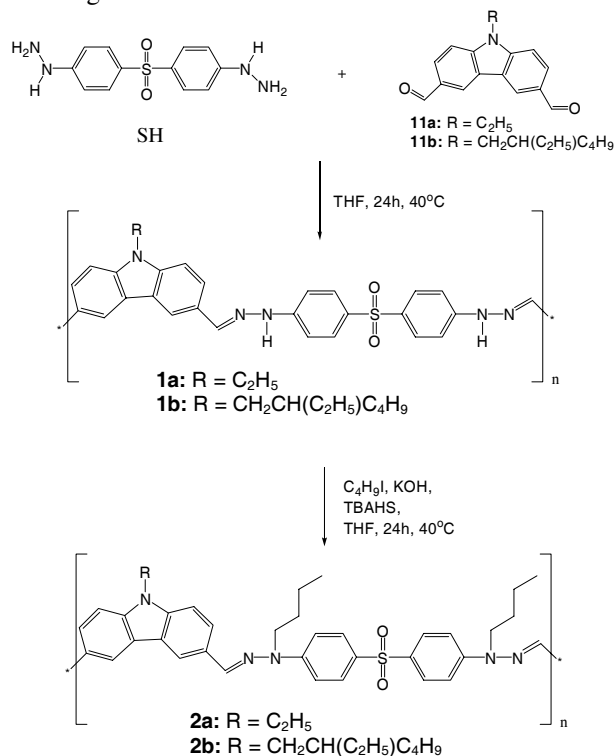


Fig. 1. Synthesis of polymers **2a** and **2b**.

The obtained polymers are soluble in common solvents like THF and chloroform. The molecular weight distribution curves of the synthesized polymers are presented in Fig. 2. The obtained molecular weight and polydispersity index values for 2a are $M_n = 3860$, $M_w = 6750$, $M_w/M_n = 1.75$ and for 2b they are $M_n = 2700$, $M_w = 4930$, $M_w/M_n = 1.83$.

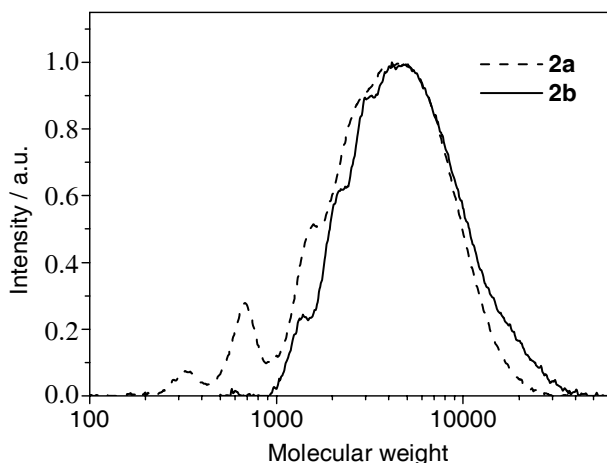


Fig. 2. Molecular weight distribution of polymers 2a and 2b.

The optical, thermal and photoelectric properties of polymers 2a and 2b were studied and compared with those of low-molar-mass glass-forming diphenylsulfone dihydrazones the chemical structures of which are presented in Fig. 3.

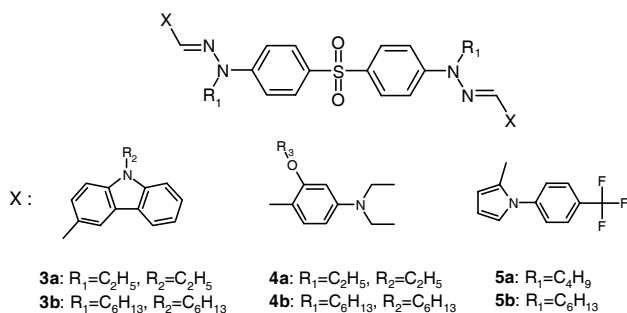


Fig. 3. Chemical structures of diphenylsulfone dihydrazones.

The optical properties of the polymeric and low-molar-mass diphenylsulfone dihydrazones were investigated by UV/VIS spectroscopy. Compounds 3a, 3b and 5a, 5b absorb in the range of 220 – 420 nm, whereas the absorption range compounds 4a, 4b and 2a, 2b is 220 – 450 nm (Fig. 4). The absorption spectra of compounds with the same chromophores but with the different alkyl substituents are very similar, therefore the spectra of the compounds with only one kind of the substituents are presented in Fig. 4. For the comparison the absorption

spectra of the starting compounds are presented in the Fig. 4. A strong bathochromical and hyperchromical shift of K bands attributed to $\pi \rightarrow \pi^*$ transitions was observed in the spectra of all compounds in comparison with the spectra of the starting compounds. This observation shows that the π -electron conjugation systems in these compounds are strongly extended and thus a relatively effective charge transport can be expected in the electrographic layers of these compounds.

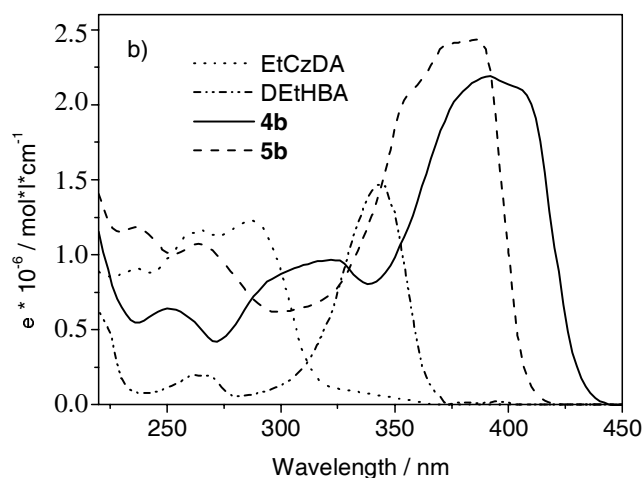
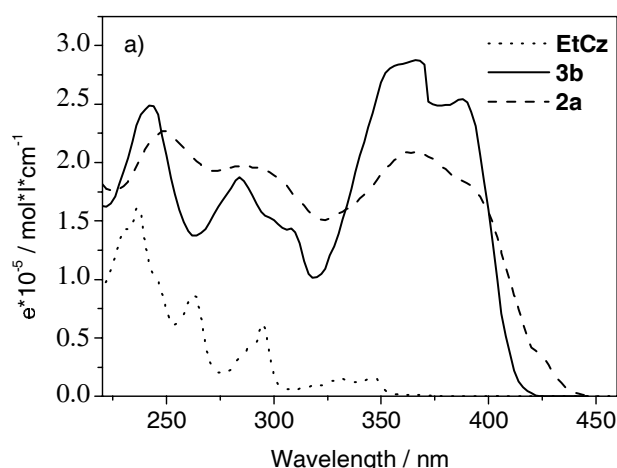


Fig. 4. UV/VIS absorption spectra of dilute solutions in THF ($c = 10^{-5}$ mol/l) of: a) compounds 2a, 3b, and 9-ethylcarbazole (EtCz), b) compounds 4b, 5b, 9-ethylcarbazole-3,6-dicarbaldehyde (ETCzDA) and 4-diethylamino-2-hydroxybenzaldehyde (DEtHBA).

TGA measurements confirmed that all the studied polymeric and low-molar-mass diphenylsulfone dihydrazones exhibit moderate thermal stability. Their 5% weight loss temperatures ($T_{dec-5\%}$) are in the range of 288 – 325 °C (Table 1). It was earlier reported that the thermal degradation of aromatic hydrazones starts from the hydrazone moiety [17]. The data obtained in this study show that the thermal stability of such compounds also depend on the nature of substituents attached to the hydrazone moiety. The

highest thermal stabilities were observed for carbazolyl-containing hydrazones i.e. for polymers 2a and 2b and their low-molar-mass models 3a and 3b. The lowest $T_{\text{dec-5\%}}$ values were observed for 4-diethylamino-2-alkoxyphenyl-substituted hydrazones (4a, 4b).

The DSC measurements revealed melting peaks in the first DSC scans of all low-molar-mass diphenylsulfone dihydrazones. A polymorphic melting was observed in the first DSC heating runs for compounds 3b, 4b and 5b. Such behaviour of large molecules inclined to form different crystalline forms was described in literature [2]. All the synthesized low-molar-mass compounds form glasses after cooling of the melted samples. Neither melting nor crystallization were revealed by the second and the following DSC scans. The glass transition temperatures (T_g) of the diphenylsulfone dihydrazones studied are given in Table 1. The T_g values of these compounds depend on the length of alkyl substituents. For example, compounds with hexyl substituents (3b and 4b) show markedly lower T_g than the corresponding compounds bearing ethyl substituents (3a and 4a). The nature of electrophores also influence T_g of the studied compounds. Carbazolyl-containing dihydrazones (3a, 3b) exhibit considerably higher T_g than 4-diethylamino-2-alkoxyphenyl-substituted hydrazones (4a, 4b) with same length of alkyl substituents.

Neither melting, nor crystallisation of polymers 2a and 2b was observed by the DSC measurements. This observation shows that these polymers are amorphous compounds. Unfortunately, the equipment used did not allow to observe the glass transitions in these polymers.

Table 1. Thermal characteristics of the polymeric and low-molar-mass diphenylsulfone dihydrazones.

Compound	$T_{\text{dec-5\%}}$, °C	T_m^a , °C	T_g , °C
2a	323	-	-
2b	325	-	-
3a	310	261	123
3b	320	105, 132	56
4a	296	95	66
4b	288	84, 97, 121	22
5a	304	156	92
5b	303	128, 151	75

^a in the first heating run of DSC only;

The ionisation potentials (I_p) of the polymeric and low-molar-mass diphenylsulfone dihydrazones measured by the electron photoemission in air range from 5.00 to 5.88 eV (Table 2). The lowest ionisation potential values (5.0 and 5.05 eV) were observed for the diphenylsulfone dihydrazones 4a and 4b. The highest ionisation potential values (5.83 and 5.88 eV) were determined for the diphenylsulfone dihydrazones 5a and 5b. This observation shows that ionisation potentials of diphenylsulfone dihydrazones can be varied in a relatively wide range by changing the formyl derivatives used in their synthesis. With respect of the I_p values of all the reported in this article compounds are suitable for the application in electrographic photoreceptors. Holes can be injected into the charge transport layer from a charge generation layer with I_p close to I_p of charge transport layer. The I_p values for charge generation materials widely used in electrographic photoreceptors such as titanyl phthalocyanines, perylene pigments and bisazo pigments are in the range of 5.1-5.6 eV [2].

Table 2. Ionisation potentials of the polymeric and low-molar-mass diphenylsulfone dihydrazones.

Compound	2a	2b	3a	3b	4a	4b	5a	5b
I_p , eV	5.55	5.40	5.33	5.28	5.05	5.00	5.88	5.83

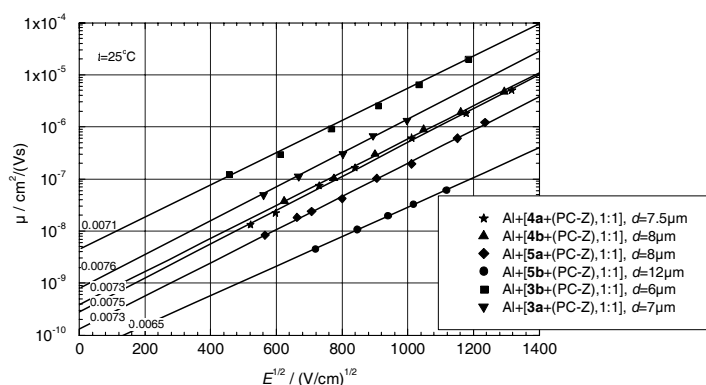


Fig. 6. Electric field dependencies of hole-drift mobilities in the films of diphenylsulfone dihydrazones 3a, 3b, 4a, 4b, 5a and 5b molecularly doped in PC-Z (50 wt.%).

The xerographic time-of-flight technique was used to estimate hole-drift mobilities in the films of the diphenylsulphone dihydrazones 3a, 3b; 4a, 4b and 5a, 5b molecularly doped in polymer host bisphenol Z polycarbonate (PC-Z) (50 wt.%). The room temperature hole-drift mobilities in these materials show linear dependencies on the square root of the electric field (Fig. 6). This observation is characteristic of the majority of non-crystalline organic semiconductors and is attributed to the effects of disorder on charge transport [12].

The hole-drift mobilities in the amorphous films of the diphenylsulphone dihydrazones doped in polymer host bisphenol Z polycarbonate (PC-Z) are in the range of 10^{-8} - 10^{-5} $\text{cm}^2/(\text{V}\cdot\text{s})$. The highest hole-drift mobility exceeding 10^{-5} $\text{cm}^2/(\text{V}\cdot\text{s})$ at high electric fields was observed in the layer of the solid solutions of diphenylsulphone dihydrazone 3b in PC-Z.

We were not able to estimate charge transport properties of polymers 2a and 2b due to their insufficient solubility.

4. Conclusions

Hole-transporting polymeric and low-molar-mass glass-forming diphenylsulfone dihydrazones have been synthesized and their optical, thermal and photoelectrical properties have been studied. The synthesized compounds absorb light in the range of 220–450 nm. The thermal decomposition of the diphenylsulfone hydrazone compounds starts above 280 °C. The diphenylsulfone dihydrazones form glasses with the glass transition temperatures ranging from 22 °C to 123 °C. The ionisation potentials of the amorphous films of the compounds are in the range of 5.00–5.88 eV. Hole-drift mobilities in the film of the solid solution of one diphenylsulfone dihydrazone in bisphenol Z polycarbonate exceed 10^{-5} $\text{cm}^2/(\text{Vs})$ at high applied electric fields as characterized by the time-of-flight method.

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