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New synthesized monohydrazone and dihydrazone containing 1-phenyl-1,2,3,4-tetrahydroquinoline moiety were investigated. The materials were examined by various techniques including differential scanning calorimetry (DSC), UV spectrometry, electron photoemission and xerographic time of flight (XTOF) techniques. The highest hole drift mobility $10^{-5}\,cm^2V^{-1}s^{-1}$ *at an electric field of* $10^6\,Vcm^{-1}$ *was observed for the dihydrazone.*

Keywords: charge transport; electrophotography; hydrazone; 1-phenyl-1,2,3,4-tetrahydroquinoline

INTRODUCTION

During recent years rapid development in the chemistry of 1,2,3,4-tetrahydroquinolines was observed. Traditionally they are of

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interest for their physiological activity. Many relatively simple synthetic of 1,2,3,4-tetrahydroquinolines are already used or have been tested as potential drugs [1,2]. Besides pharmaceutical applications, tetrahydroquinoline derivatives are useful as corrosion inhibitors [3], antioxidants [4], active components of various dyes [5] and pesticides [6]. They are also widely used in modern recording technologies: as intermediates for photographic couplers [7], as highly sensitive photosensitizers in photography [8] and as charge transporting materials in electrophotographic photoconductors [9].

Compounds possessing hydrazone moiety are also well known for their photoresponsible properties [10]. Due to high photosensitivity, simple synthesis and low price they gain the advantage over other hole transporting materials. Low molecular weight transporting materials (TM) containing hydrazone moiety are usually crystalline substances, not capable of forming thin neat homogenous layers, and therefore must be used in combination with polymeric hosts, usually polycarbonate (PC). Aromatic hydrazone molecules dispersed in a binding polymer are used as the main constituent of electrophotographic devices due to their excellent hole transporting ability [11]. Recently, organic photoreceptors with hydrazones possessing 1-phenyl-1,2,3,4-tetrahydroquinoline moiety were recognized as hole transporting materials due to their rapid charge transporting ability [12]. Unfortunately, the time and labour consuming multistep synthesis of starting 1-phenyl-1,2,3,4-tetrahydroquinoline limits the development of organic photoreceptors with this promising moiety.

In the present article we report the synthesis, characterization and photoconductive properties of hydrazones **4a** and **4b** possessing 1-phenyl-1,2,3,4-tetrahydroquinoline moiety. The molecules of these TM include the large π-electron system conjugated through nitrogen atoms and the flexible tetrahydroquinoline core with methoxy group attached to it. These TM showed themselves as excellent hole transporting materials: the measured mobilities of new **4a,b** are high enough for many practical applications.

EXPERIMENTAL

3-Hydroxy-1-Phenyl-1,2,3,4-Tetrahydroquinoline (1). Synthesis of the starting 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline **1** was carried out according to the procedure described in [13].

3-Methoxy-1-Phenyl-1,2,3,4-Tetrahydroquinoline (2). The mixture of 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline **1** (22.5 g, 0.1 mol), iodomethane (31.1 ml, 0.5 mol), potassium hydroxide (13.2 g, 0.02 mol) and potassium carbonate (13.8 g, 0.1 mol) was refluxed for 4 hours. At the end of the reaction potassium hydroxide, potassium

carbonate and potassium iodide were filtered off. The filtrate was extracted with chloroform and washed with H_2O until neutral. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed *in vacuo* together with the unreacted iodomethane. The obtained compound **2** was used in the next step without purification.

3-Methoxy-1-Phenyl-1,2,3,4-Tetrahydroquinoline-6-Carboxaldehyde (3a). To a 250 ml 3-neck round bottom flask equipped with thermometer, magnetic stirrer and addition funnel, was added DMF (46.5 ml, 0.6 mol). The content was cooled down in a salt/ice bath, and 18.5 ml of $POCl_3$ (0.2 mol) were added portionwise, not allowing the temperature of the mixture to rise above 5°C. After the addition was completed, the reaction mixture was allowed to warm to room temperature. A solution of compound **2** (23.9 g, 0.1 mol) in 50 ml of DMF was then added. The mixture was heated at 90°C for 1 h. The hot reaction mixture was poured into a 500 ml beaker containing 200 g ice. The mixture was neutralized by adding 40% NaOH and allowed to stand at 5°C for 24 hours. The precipitate was decanted, dissolved in ethyl acetate, the solution was washed with H_2O until neutral, dried over anhydrous $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel using n-hexane/acetone = 7:1 as the eluent. The pure product **3a** was collected and dried in vacuum at 30°C (17.4 g, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 9.70 (s, 1H, CHO); 7.62–7.23 (m, 7H, Ar); 6.54 (d, 1H, $J = 8.6$ Hz, 8-H of quinoline ring); 3.95–3.87 (m, 1H, CH); 3.86–3.64 (m, 2H, NCH_2); 3.43 (s, 3H, CH_3); 3.16 (dd, 1H, $J_{AB} = 16.0$ Hz, $J_{AX} = 4.1$ Hz, H_A of CH_2CH); 3.00 (dd, 1H, $J_{BX} = 6.3$ Hz, Hz, H_B of CH_2CH). IR, ν/cm^{-1}: 3061, 3037 (CH_{Ar}); 2980, 2930, 2895 ($CH_{aliph.}$); 1674 (CHO); 965, 818, 772, 701 (CH=CH of mono- and trisubstituted benzenes). Found, %: C 76.25; H 6.35; N 5.16. $C_{17}H_{17}NO_2$. Calculated, %: C 76.38; H 6.41; N 5.24.

1-(4-Formylphenyl)-3-Methoxy-1,2,3,4-Tetrahydroquinoline-6-Carboxaldehyde (3b). Compound **3b** was prepared according to the preparation procedure described above for **3a**, except that much bigger amounts of DMF (228 ml, 2.94 mol) and $POCl_3$ (129 ml, 1.4 mol) were used, and reaction time was prolonged to 24 hours. The crude product was purified by column chromatography to give 12 g of compound **3b** (40% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 9.95 (s, 1H, CHO in Ph), 9.79 (s, 1H, CHO in quinoline ring); 7.94–7.21 (m, 6H, Ar); 7.02 (d, 1H, $J = 8.5$ Hz, 8-H of quinoline ring); 3.98–3.66 (m, 3H, NCH_2CH); 3.37 (s, 3H, CH_3); 3.15 (dd, 1H, $J_{AB} = 16.2$ Hz, $J_{AX} = 4.3$ Hz, H_A of CH_2CH); 3.01 (dd, 1H, $J_{BX} = 5.6$ Hz, H_B of CH_2CH). IR, ν/cm^{-1}: 3064, (CH_{Ar}); 2934, 2897, 2827 ($CH_{aliph.}$); 1677 (CHO). Found, %: C 73.15; H 5.82; N 4.72. $C_{18}H_{17}NO_3$. Calculated, %: C 73.20; H 5.80; N 4.74.

3-Methoxy-1-Phenyl-1,2,3,4-Tetrahydroquinoline-6-Carboxaldehyde N,N-Diphenylhydrazone (4a). To a solution of N,N-diphenylhydrazine hydrochloride (2.4 g, 11 mmol) in 80 ml of methanol was added a solution of compound **3a** (2 g, 7 mmol) in 15 ml of methanol. The mixture was refluxed for 1 h. Then the reaction mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, and organic solvents were removed. The residue was purified by column chromatography on silica gel using n-hexane/ethyl acetate = 7:1 as the eluent. The pure product was crystallized from the eluent, filtered off and recrystallized from ethyl acetate/methanol = 1:1 to yield 1.6 g (49%). m.p.: 140.5–142°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.43–7.07 (m, 18H, Ar and CH=N); 6.69 (d, 1H, J = 8.6 Hz, 8-H of quinoline ring); 3.88–3.77 (m, 1H, CH); 3.77–3.50 (m, 2H, NCH_2); 3.39 (s, 3H, CH_3); 3.12 (dd, 1H, $J_{AB} = 16.1$ Hz, $J_{AX} = 4.6$ Hz, H_A of CH_2CH); 3.00 (dd, 1H, $J_{BX} = 7.0$ Hz, H_B of CH_2CH). Found, %: C 80.26; H 6.32; N 9.72. $C_{29}H_{27}N_3O$. Calculated, %: C 80.34; H 6.28; N 9.69.

1-(4-Formylphenyl)-3-Methoxy-1,2,3,4-Tetrahydroquinoline-6-Carboxaldehyde bis(N,N-Diphenylhydrazone) (4b). To a solution of N,N-diphenylhydrazine hydrochloride (2.6 g, 12 mmol) in 50 ml of methanol was added a solution of compound **3b** (1.5 g, 5 mmol) in 10 ml of THF. The mixture was refluxed for 1.5 h, cooled down and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, and organic solvents were removed. The residue was purified by column chromatography (n-hexane/ethyl acetate = 12:1). The product was crystallized from toluene/methanol = 2:1. The crystalline **4b** was filtered off, washed with small amount of cold methanol (5°C) and recrystallized from toluene/methanol = 2:1 (2 g, 61% yield). m.p.: 216–218°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.62–7.07 (m, 28H, Ar, CH=N); 6.81 (d, 1H, $J = 8.6$ Hz, 8-H of quinoline ring); 3.88–3.79 (m, 1H, NCH_2CH); 3.78–3.52 (m, 2H, NCH_2); 3.37 (s, 3H, CH_3); 3.12 (dd, 1H, $J_{AB} = 16.2$ Hz, $J_{AX} = 4.8$ Hz, H_A of CH_2CH); 2.87 (dd, 1H, $J_{BX} = 6.9$ Hz, Hz, H_B of CH_2CH). IR, ν/cm^{-1}: 3061, 3035 (CH_{Ar}); 2989, 2888, 2821 ($CH_{aliph.}$); 1590, 1522 (C=C, C–N). Found, %: C 80.32; H 5.89; N 11.19. $C_{42}H_{37}N_5O$. Calculated, %: C 80.36; H 5.94; N 11.16.

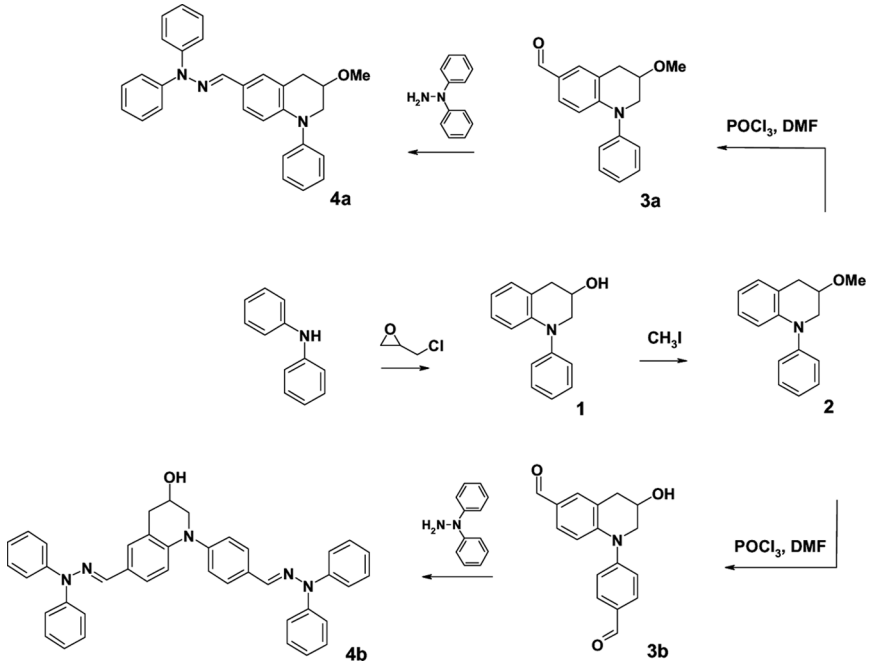
Measurement

The ^{1}H NMR spectra were taken on Varian Unity Inova (300 MHz) spectrometer in $CDCl_3$. The IR spectra were taken for samples in KBr pellets on a Perkin Elmer Spectrum BX II FT-IR System spectrometer. The UV spectra were recorded on a Spectronic Genesys 8 spectrometer in THF (10^{-4} M) in a microcell with an internal width

of 1 mm. The course of the reactions and the purity of the products were monitored by TLC on Silufol UV-254 plates (eluent: n-hexane/acetone = 3/1) and development with I_2 or UV light. Silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) was used for column chromatography. Elemental analyses were performed with an Exeter Analytical CE-44 Elemental Analyzer. Thermal transition data for synthesized compounds **4a** and **4b** was collected using a TA Instruments Model 2929 apparatus (New Castle, DE) at a heating rate of 10 K/min under nitrogen atmosphere. The glass transition temperatures (T_g) were determined from the second heating. Ionization potential was measured by the photoemission in air method described in [14]. The samples for mobility measurements were prepared from 1:1 mass proportion compositions of **4a** and **4b** with polycarbonate-Z (PC) (Iupilon Z-200 from Mitsubishi Gas Chemical Co.). The sample substrate was polyester film with conductive Al layer. The layer thickness was in the range of 7–11 μm. The hole drift mobility was measured by XTOF technique [15]. Positive corona charging created electric field inside the TM layer. Charge carriers were generated at the layer surface by illumination with pulses of N_2 laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5% of the initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the rate of the surface potential decrease, dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in linear scale. The drift mobility was calculated by the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness and U_0 is the surface potential at the moment of illumination.

RESULTS AND DISCUSSION

A practical route for the synthesis of hydrazones **4a** and **4b** possessing 1-phenyl-1,2,3,4-tetrahydroquinoline moiety is shown in Scheme 1. Differently to the multi-step synthesis of the widely used 1-phenyl-1,2,3, 4-tetrahydroquinoline, the starting 3-hydroxy-1-phenyl-1,2, 3,4-tetrahydroquinoline **(1)** was obtained by one-pot reaction of diphenylamine with epichlorohydrin as described in [13]. Alkylation of **1** with iodomethane in the presence of KOH and K_2CO_3 gave phenyltetrahydroquinoline **2** substituted with methoxy group. The next step was a Vilsmeier formylation followed by condensation of the resulting monoaldehyde **3a** and dialdehyde **3b** with N,N-diphenylhydrazine to get final products-hydrazones **4a** and **4b**. The chemical structures of the new hole transporting compounds **4a** and **4b** were confirmed by IR, UV, ^{1}H NMR spectrometry and elemental analysis.



SCHEME 1 Synthesis of researched material.

The formation of the glassy state in **4a** and **4b** was confirmed by DSC. The melting points (T_m) and glass transition temperatures (T_g) of the synthesized TM are presented in Table 1. These investigations revealed, that products **4a,b** exist both in crystalline and amorphous state. Figure 1 shows, that the DSC curve for **4a** at first heating reveals two peaks, corresponding to two eutectic melting points at 125°C and 142°C. Thus, hydrazone **4a** is distinguished by polymorphism with the predominant second crystalline phase at 142°C. No crystallization takes place during second heating, only glass transition is revealed at 44°C. The material remains in glassy state after melting and subsequent cooling. This is also common for

TABLE 1 Characteristics of **4a** and **4b**

Compound	T_m/°C	T_g/°C	I_p/eV	$\mu_0/cm^2V^{-1}s^{-1}$	$\mu/cm^2V^{-1}s^{-1}$
4a	142	44	5.29	$2 \cdot 10^{-7}$	$7.2 \cdot 10^{-6}$
4b	214	81	5.21	$5.6 \cdot 10^{-7}$	$2.2 \cdot 10^{-5}$

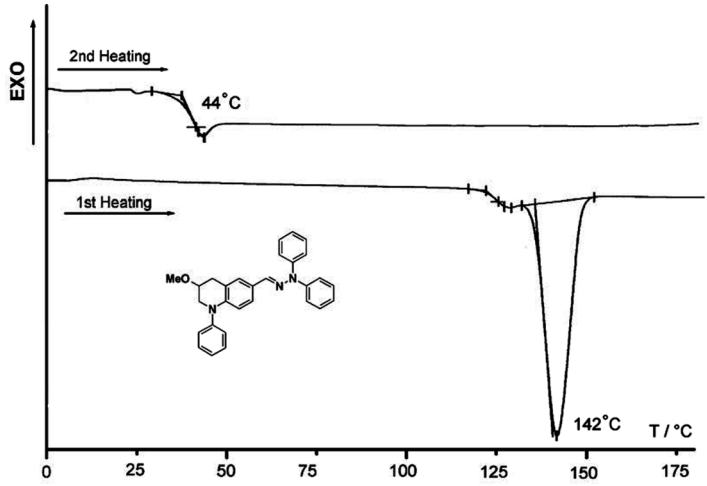


FIGURE 1 DSC curves for **4a** (heating rate to 10 K/min).

monocrystalline material **4b**, except that this molecular glass exhibits higher $T_g = 81$°C.

Since π-electrons are very important for the charge transporting process in the TM structures, the absorption spectra of **4a** and **4b** were recorded. Figure 2 demonstrates that electron transitions to the higher energy states in the investigated derivatives give two main absorption maxima at *ca*. 210 nm and 380 nm. The comparison of **4a** and **4b** with the starting **1** showed, that the second absorption band is bathochromically shifted by 72 nm and 98 nm respectively, because of the π-electron conjugation including the lone electron pair on the nitrogen atom. Furthermore, dihydrazone **4b**, as compared to monohydrazone **4a**, showed additional 26 nm shift to longer wavelengths due to expanded conjugated π-electrons system.

The results of the electron photoemission in air are presented in Figure 3. There is a little ionization potencial (I_p) difference between monohydrazone **4a** and dihydrazone **4b** (Table 1). The ionization potential value for compound **4a** is 5.29 eV. As expected, $I_p = 5.21$ eV for the compound **4b** is lower if compared to **4a**. It is known, that the I_p values for charge transporting materials, including those widely used with pigments in electrophotographic photoreceptors, such as titanyl phthalocyanines [16], are in the range of 5.1–5.6 eV. Thus, I_p values of the newly synthesized **4a,b** are sufficient for these compounds to be used as charge transporting materials.

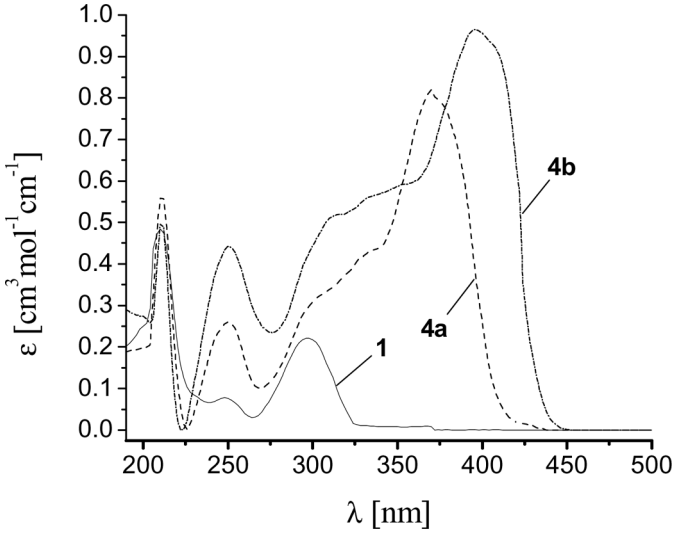


FIGURE 2 Absorption spectra (THF, $c = 10^{-4}$ M) of **4a**, **4b** and starting compound **1**.

Investigative 1-phenyl-1,2,3,4-tetrahydroquinoline based hydrazones **4a,b** are soluble in common organic solvents such as acetone, chloroform, THF, dioxane etc. This really good solubility is mainly due to the flexible tetrahydroquinoline core in **4a** and **4b**. Clear, transparent and

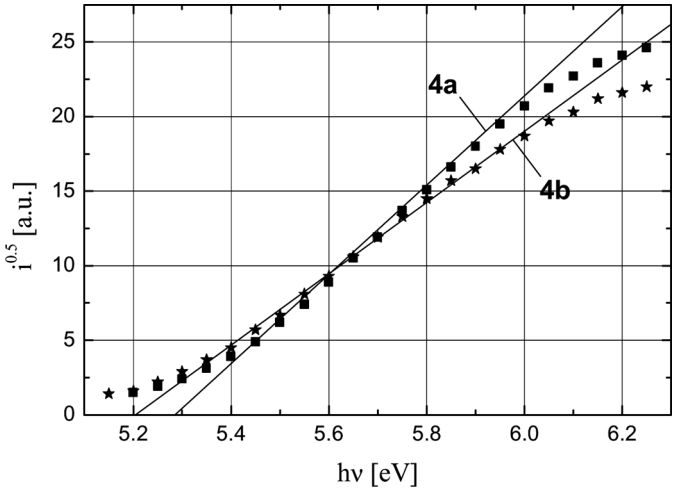


FIGURE 3 Photoemission (in air) spectra of the TM.

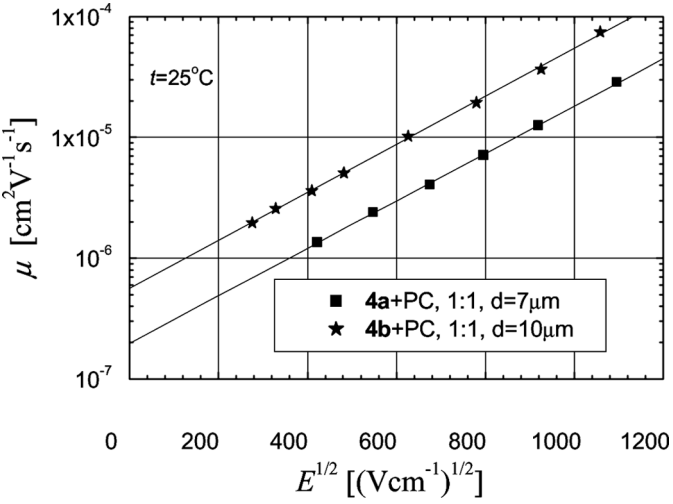


FIGURE 4 Field dependencies of the hole drift mobilities of **4a** and **4b**.

homogeneous films were obtained by the casting technique. The hole drift mobility for the investigative TM **4a** and **4b** was measured by XTOF technique.

Figure 4 shows the room temperature dependencies of hole drift mobility on electric field for **4a** and **4b** in the composition with PC. The mobility defining parameters μ_0 and the mobility value at the $6.7 \cdot 10^5\,\mathrm{Vcm}^{-1}$ field are given in Table 1. Mobility value in amorphous film of the composition of **4b** with PC exceeds $10^{-5}\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ at an electric field of $10^6\,\mathrm{Vcm}^{-1}$. As seen from these results, hole drift mobility of **4b** is by one order of magnitude higher than mobility of **4a**. This is presumable because conjugated π-electron system is larger in the compound **4b**. It should be noted, that the measured mobility of the TM compositions with a binder is high enough for many practical applications and it remains approximately in the same range as was reported for compound 1-phenyl-1,2,3,4-tetrahydroquinoline-6-carboxaldehyde-1,1′-diphenylhydrazone [17].

CONCLUSIONS

A simple synthesis procedure of 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline allows to develop and evaluate novel hole transporting materials possesing phenyl-1,2,3,4-tetrahydroquinoline moiety for electrophotography. DSC investigations revealed, that the newly synthesized hydrazones **4a** and **4b** can exist both in crystalline and

amorphous state. The measured mobilities of the TM are high enough for many practical applications. The highest hole mobility exceeding $10^{-5}\,cm^2V^{-1}s^{-1}$ at an electric field of $10^6\,Vcm^{-1}$ was observed in the case of **4b**.

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