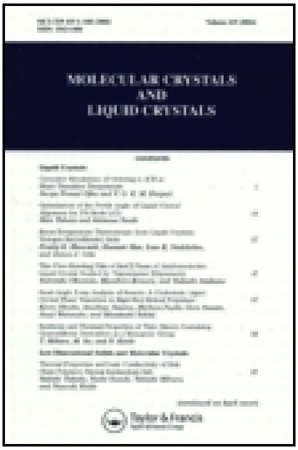

Molecular Crystals and Liquid Crystals

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Electron Transporting Molecular Glasses Based on Arylmethylene-1,3-Indandione

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Arylmethylene-1,3-indandione-based molecular glasses were synthesized starting from 1,3-indandione. These compounds were found to constitute novel charge transporting materials and were examined by various techniques including differential scanning calorimetry, electron photoemission, cyclic voltammetry, and xerographic time-of-flight techniques. The electron photoemission spectra of the layers showed the ionization potentials of 5.8–5.9 eV. The cyclic voltammograms and the charge carrier mobilities measured by the time-of-flight technique confirm that synthesized molecular glasses are n-channel organic semiconducting materials. The electron drift mobility exceeds $10^{-8}\,cm^2\,V^{-1}\,s^{-1}$ *at strong electric fields.*

Keywords: 1,3-indandione; charge transport; electron drift mobility; ionization potential; molecular glasses

INTRODUCTION

A wide range of π-conjugated organic materials has been recently tested for the manufacturing of organic optoelectronic devices (OED). In order to have efficient devices of such a type for commercial applications, the most important requirement is to balance the hole

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and electron injections and to have the sufficient carrier mobility of both charge carriers. This means, in turn, that one needs to look for materials which possess the desirable ionization potential for hole transporting materials and the electron affinity for electron transporting ones. So far, the development of hole-transporting and bipolar materials has been superior to electron transporting ones [1]. The aryl(hetero)methylene-1,3-indandiones is a promising class of bipolar compounds exhibiting the high hyperpolarizability, intramolecular charge transfer ability, and excellent photoconductivity which are important for a possible use of these compounds in an active medium of OED [2–5]. Materials based on 1,3-indandione are also candidates for the application as electron transporting materials [6–8].

Low molecular aryl(hetero)methylene-1,3-indandiones are usually crystalline materials. They may form uniform transparent thin films by vapor deposition in vacuum and are not capable to form thin neat homogeneous layers from solutions by spin-coating methods. Such materials need to be used with polymeric binders. Even in such compositions, the possibility of the crystallization of aryl(hetero)methylene-1,3-indandiones remains and causes problems during the OED preparation and the long-time usage, because low-molecular-weight compounds possessing 1,3-indandione moieties generally tend to form crystals. It is of interest and significance to develop photo- and electroactive low-molecular-weight amorphous materials that form stable amorphous glasses having glass-transition temperatures above room temperature [9]. These molecular glasses form stable films without polymeric host materials and are expected to have better properties as compared with molecularly doped polymer compositions. Molecular glasses are already used in technical applications and can be regarded as attractive candidates for some newly developing fields. They are used as charge-transporting and/or emitting materials in light-emitting diodes, electrophotographic materials, and photovoltaic devices [10,11]. As photoconductive or multifunctional materials they can be used in photorefractive systems [12]. Molecular glasses are also candidates for the application as electrically conducting materials [13], photochromic materials [9], and resist materials for electron-beam lithography [14].

In the previous contributions, we have reported the synthesis of a novel class of low-molar-mass compounds which are capable to exist in amorphous state. We prepare such compounds by the reactions of oxiranes containing electroactive groups with different difunctional compounds such as aromatic diols, dimercapto compounds, and derivatives of anilines [15–17]. In the course of these findings, we put our efforts to the synthesis of an indandione moiety containing molecular glasses [18].

In the present work, we describe the synthesis and characterization of arylmethylene-1,3-indandione-based molecular glasses. An increase of the molar mass usually leads to an increase of the stability of molecular glasses. In addition, the molecules of these compounds consist of two 2-(naphthalene-1-ylmethylene)-1,3-indandione branches linked by a central flexible bridge. This circumstance should also enhance the predisposition of the designed molecules to form glasses.

EXPERIMENTAL

Materials

1-Chloro-2,3-epoxypropane, 4,4′-thiobisbenzenethiol, 1,3-benzenedithiol, 2-hydroxy-1-napthaldehyde, and 1,3-indandione were purchased from "Aldrich" and used without additional purification.

2-Oxiranylmethoxy-1-naphthaldehyde (1)

15 g (87 mmole) of 2-hydroxy-1-napthaldehyde, 1.98 g (8.7 mmole) of benzyl triethylammonium chloride, and 345 ml (4.35 mole) of epichlorohydrin were placed into a round bottom flask. The reaction mixture was intensively stirred at the reflux temperature for 15 min. After the termination of the reaction (TLC, acetone: *n*-hexane, 7:18), the reaction mixture was treated with chloroform and washed with distilled water. The organic layer was dried over anhydrous $MgSO_4$, filtered, and solvent and excess of epichlorohydrin were removed. The residue was treated with 2-propanol. The obtained crystals were filtered off and washed with 2-propanol. The yield was 79% (16.5 g) (m.p.: 102–104°C (2-propanol)). IR (KBr), $\bar{\nu}$, cm^{-1}: 3064 (CH$_{\text{arom}}$), 2997, 2926, 2878, 2799 (CH$_{\text{aliph}}$), 1667 (C=O), 1618, 1592, 1565, 1513 (C=C), 1268, 1250, 1154, 1060 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 10.91 (s, 1H, HC=O); 9.25 (d, $J = 8.5$ Hz, 1H, 8-H Naph$_{1,2\text{-subst.}}$); 8.01 (d, $J = 9.2$ Hz, 1H, 4-H Naph$_{1,2\text{-subst.}}$); 7.75 (d, $J = 8.1$ Hz, 1H, 5-H Naph$_{1,2\text{-subst.}}$); 7.64–7.56 (m, 1H, 7-H Naph$_{1,2\text{-subst.}}$); 7.45–7.37 (m, 1H, 6-H Naph$_{1,2\text{-subst.}}$); 7.23 (d, $J = 9.2$ Hz, 1H, 3-H Naph$_{1,2\text{-subst.}}$); 4.48 (dd, $J_{AM} = 11.2$ Hz, $J_{AX} = 2.9$ Hz, (H$_A$), 1H, one of CH$_2$O protons); 4.16 (dd, $J_{MA} = 11.2$ Hz, $J_{MX} = 5.7$ Hz, (H$_M$), 1H, another of CH$_2$O protons); 3.45–3.38 (m, 1H, (H$_X$), CHO); 2.94 ((t, $J_{A'M'} = 4.5$ Hz, (H$_{A'}$), 1H, one of CH$_2$O protons); 2.79 (dd, $J_{M'A'} = 4.5$ Hz, $J_{M'X} = 2.6$ Hz, (H$_{M'}$), 1H, another of CH$_2$O protons). Elemental analysis. Calcd. for $C_{14}H_{12}O_3$ (%): C 73.67; H 5.30. Found (%): C 73.55; H 5.10.

2-Oxiranylmethoxy-1-(1,3-dioxoindan-2-ylmethylene)naphthalene (2)

To a 250-ml round bottom flask, 13.15 g (58 mmole) of 2-(2-oxiranylmethoxy)-1-naphthaldehyde, 8.42 g (58 mmole) of 1,3-indanedione and 145 ml of ethanol were added. The reaction mixture was stirred at room temperature for 96 h. The obtained light orange crystals were filtered off and washed with *2*-propanol and diethyl ether. The yield was 88% (18 g) (m.p.: 184–186°C (THF: *2*-popanol, 1:1)). IR (KBr), $\bar{\nu}$, cm^{-1}: 3047 (CH_{arom}), 2999, 2950, 2883, 2799 (CH_{aliph}), 1726, 1688 (C=O), 1608, 1588, 1513 (C=C) 1267, 1252, 1218, 1158, 1056 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 8.37 (s, 1H, Naph–CH=C); 8.05–7.99 (m, 1H, 4-H $Naph_{1,2\text{-subst.}}$); 7.94–7.84 (m, 2H, 5-H, 8-H $Naph_{1,2\text{-subst.}}$); 7.81–7.69 (m, 4H, $Ph_{1,2\text{-subst.}}$); 7.48–7.41 (m, 1H, 7-H $Naph_{1,2\text{-subst.}}$); 7.39–7.32 (m, 1H, 6-H $Naph_{1,2\text{-subst.}}$); 7.26 (d, $J = 9.2$ Hz, 1H, 3-H $Naph_{1,2\text{-subst.}}$), 4.34 (dd, $J_{AM} = 11.0$ Hz, $J_{AX} = 3.2$ Hz, (H_A), 1H, one of Ph-O-CH_2 protons); 4.10 (dd, $J_{MA} = 11.0$ Hz, $J_{MX} = 5.6$ Hz, (H_M), 1H, another of Ph-O-CH_2 protons); 3.21–3.15 (m, 1H, CHO); 2.73 (t, $J_{A'M'} = 4.9$ Hz, ($H_{A'}$), 1H, one of O-CH_2 of oxirane protons); 2.63 (dd, $J_{M'A'} = 4.9$ Hz, $J_{M'X} = 2.7$ Hz, ($H_{M'}$), 1H, another of O-CH_2 of oxirane protons). Elemental analysis. Calcd. for $C_{23}H_{16}O_4$ (%): C 77.52; H 4.53. Found (%): C 77.44; H 4.48.

4,4′-Bis-{{3-hydroxy-4-[1-(1,3-dioxoindan-2-ylmethylene) naphthalen-3-yloxy]-1-thiabutyl}phenyl}sulfide (3a)

Compound **2** (4 g, 11.22 mmole) and 4,4′-thiobisbenzenedithiol (1.12 g, 4.5 mmole) were dissolved in 60 ml of THF. Then 0.24 ml (1.8 mmole) of triethylamine was added. The mixture was stirred intensively at the reflux temperature for 30 min. After the termination of the reaction (TLC, acetone: *n*-hexane, 7:18), solvent was evaporated. The residue was purified by column chromatography using 2:3 acetone: *n*-hexane as the eluent. The resultant oil was dissolved in 20 ml of THF and then precipitated with intensive stirring into 300 ml *n*-hexane. The yield was: 63% (4.3 g). IR (KBr), $\bar{\nu}$, cm^{-1}: 3455 (OH), 3055 (CH_{arom}), 2927, 2872, (CH_{aliph}), 1706, 1687 (C=O), 1620, 1592, 1549, 1512 (C=C) 1268, 1247, 1156, 1098 (C−O−C), 808, 508 (*para* subst. benzene). ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 8.42 (m, 2H, Naph–CH=C); 8.06–7.01 (m, 28H, Ar); 4.40–4.16 (m, 4H, OCH_2); 3.68 (d, $J = 5.7$ Hz, 2H, OH); 3.50–3.05 (m, 6H, $CHCH_2S$). Elemental analysis. Calcd. for $C_{58}H_{42}O_8S_3$ (%): C 72.33; H 4.40. Found (%): C 72.35; H 4.37.

1,3-Bis-{3-hydroxy-4-[1-(1,3-dioxoindan-2-ylmethylene)naphthalen-3-yloxy]-1-thiabuthyl}-benzene (3b)

Compound **2** (4.5 g, 12.5 mmole) and benzene-1,3-dithiol (0.85 g, 6 mmole) were dissolved in 60 ml of THF. Then 0.33 ml (2.4 mmole) of triethylamine was added. The mixture was stirred intensively at the reflux temperature for 1 h. After the termination of the reaction (TLC, acetone: *n*-hexane, 7:18), solvent was evaporated. The residue was purified by column chromatography using 2:3 acetone: *n*-hexane as the eluent. The resultant oil was dissolved in 25 ml of THF and then precipitated with intensive stirring into 400 ml of *n*-hexane. The yield was 63% (3.23 g). IR (KBr), $\bar{\nu}$, cm^{-1}: 3454 (OH), 3055 (CH$_{\mathrm{arom}}$), 2927, 2872, (CH$_{\mathrm{aliph}}$), 1707, 1686 (C=O), 1620, 1592, 1513 (C=C) 1246, 1250, 1154, 1060 (C-O-C), 739, 510 (*m*-subst. benzene). ^{1}H NMR (300 MHz, CDCl$_3$), δ, ppm: 8.35 (m, 2H, Naph–CH=C); 8.17–6.92 (m, 24H, Ar); 4.40–4.96 (m, 4H, OCH$_2$); 3.60 (d, $J = 5.3$ Hz, 2H, OH); 3.45–3.95 (m, 6H, CHCH$_2$S). Elemental analysis. Calcd. for $C_{52}H_{38}O_8S_2$ (%): C 73.05; H 4.48. Found (%): C 73.20; H 4.56.

1,3-Bis-{3-acetyl-4-[1-(1,3-dioxoindan-2-ylmethylene)-naphthalen-3-yloxy]-1-thiabuthyl}-benzene (3c)

Compound **3b** (2 g, 2.3 mmole) was dissolved in 20 ml of acetic acid anhydride. The mixture was heated at 85°C for 19 h. After the termination of the reaction (TLC, acetone: *n*-hexane, 7:18), the reaction mixture was treated with ethyl acetate and washed with distilled water. The organic layer was dried over anhydrous MgSO$_4$, filtered, and solvent was removed. The residue was purified by column chromatography using 1:4 acetone: *n*-hexane as the eluent. The resultant oil was dissolved in 10 ml of THF and then precipitated at the intensive stirring into 200 ml of *n*-hexane. The yield was 62% (1.36 g). IR (KBr), $\bar{\nu}$, cm^{-1}: 3443 (OH), 3056 (CH$_{\mathrm{arom}}$), 2933, (CH$_{\mathrm{aliph}}$), 1740 (OC=O), 1711, 1690 (C=O), 1590, 1571, 1513 (C=C) 1226 (C−O−C), 739, 510 (*m*-subst. benzene). ^{1}H NMR (300 MHz, CDCl$_3$), δ, ppm: 8.33 (m, 2H, Naph–CH=C); 8.07–6.92 (m, 24H, Ar); 4.35–4.91 (m, 4H, OCH$_2$); 3.55 (d, $J = 5.3$ Hz, 2H, OH); 3.40–3.90 (m, 6H, CHCH$_2$S); 1.89–1.82 (m, 6H, CH$_3$). Elemental analysis. Calcd. for $C_{56}H_{42}O_{10}S_2$ (%): C 71.62; H 4.51. Found (%): C 71.55; H 4.59.

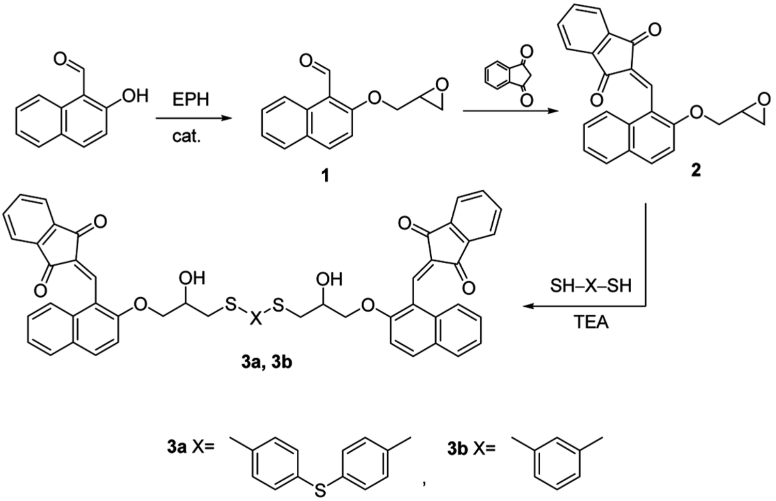
MEASUREMENT

The ^{1}H NMR spectra were recorded using a Varian Unity Inova (300 MHz) spectrometer, the chemical shifts are expressed in ppm, downfield from tetramethylsilane (TMS) used as the internal standard. The symbols d, m, t, and s are used, respectively, for doublet, multiplet, triplet, and singlet. The IR spectra were taken for samples in KBr pellets on a Perkin Elmar Spectrum GX FT-IR system spectrometer. The UV spectra were recorded on a Spectronic Genesis 8 spectrometer. 10^{-4} M solutions of the investigated materials in THF and the microcells with an internal width of 2 and 10 mm were used, respectively. X-ray diffraction was recorded using a DRON-6 diffractometer. The course of the reactions was monitored by TLC on Silufol UV-254 plates (eluent: *n*-hexane:acetone, 3:1), and the development with I_2 or UV light. Silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) was used for column chromatography. The differential scanning calorimetry (DSC) measurements were recorded on a Mettler DSC 30 calorimeter at a scan rate of 10 K/min. The ionization potential I_p was measured by the method of electron photoemission in air as described in [15]. The samples for the ionization potential measurement were prepared by dissolving materials in THF and were coated on Al plates precoated with a ~0.5-μm-thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5–1 μm. The charge carrier mobilities were measured by the time-of-flight technique [15]. Cyclic voltammograms were recorded with the equipment consisting of a Princeton Applied Research model 263A potentiostat/galvanostat. Measurements were carried out under argon at 25±2°C. Tetrabutylammonium perchlorate ($TBAClO_4$) solution in acetonitrile (0.1 mole dm^{-3}, 10 cm^3) was used as the electrolyte solution. A three-electrode system was used. The three electrodes consisted of an Ag/Ag+ reference electrode (silver wire in a 0.01 mole dm^{-3} silver nitrate solution as the electrolyte solution), a platinum working electrode (2-mm-diameter smooth platinum disk, area $= 3.14 \times 10^{-2}$ cm^2), and a platinum counter electrode (platinum wire). Thin films of the compounds were formed by drop-casting 1.0 mm^3 of their solution in dichloromethane (HPLC grade) (1 mg cm^{-3}) onto the working electrode and then drying in air. Ferrocene was employed as the reference redox system according to IUPAC's recommendation [19].

RESULTS AND DISCUSSION

The synthesis route to arylmethylene-1,3-indandione derivatives **3a** and **3b** possessing naphthalene moieties and two hydroxyl groups in the flexible bridge is shown in Scheme 1.

In general, aromatic aldehydes react with 1,3-indandione to yield *Knoevenagel* or *Michael* type adducts [20]. Intermediate 2-oxyranylmetoxy-1-naphthaldehyde (**1**) was produced by the

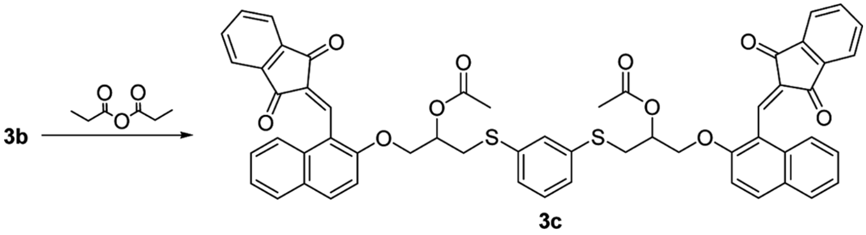


SCHEME 1 Synthesis route to 1,3-indandione derivative **3a** and **3b**.

condensation of starting 2-hydroxy-1-naphthaldehyde with epichlorohydrin. The condensation of the former aldehyde **1** with 1,3-indandione at room temperature even in the absence of a catalyst leads to the molecule **2** possessing epoxy group. The goal molecular glasses **3a** and **3b** containing indan-1,3-dione moieties were synthesized by the reaction of oxirane **2** with difunctional nucleophilic linking agents 4,4′-thiobisbenzenethiol and 1,3-benzenedithiol in the presence of a catalytic amount of triethylamine (TEA).

Compound **3b** was acylated with acetic acid anhydride, and than **3c** possessing protected hydroxyl groups was synthesized (Scheme 2).

All our attempts to crystallize **3a**, **3b**, and **3c** were unsuccessful. The obtained materials were purified by column chromatography with the following precipitation. The chemical structures of **3a**, **3b**, and **3c**



SCHEME 2 Synthesis route to 1,3-indandione derivative **3c**.

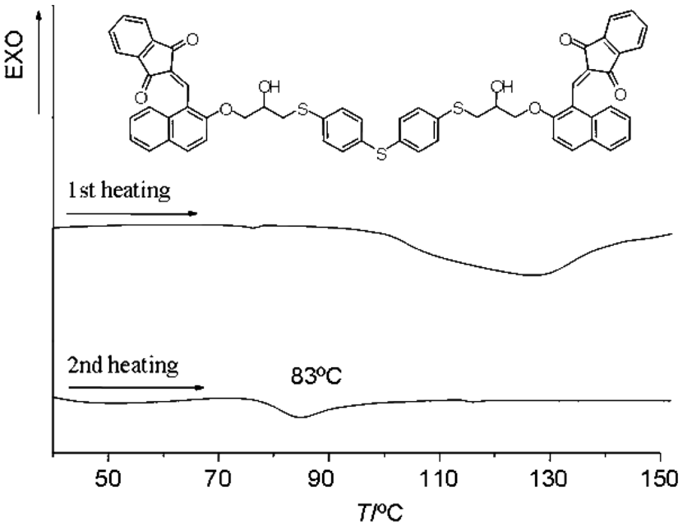


FIGURE 1 DSC curves for **3a** (heating rate to 10 K/min).

were confirmed by IR, ^{1}H NMR, and UV/Vis spectroscopy. Some individual downfield peaks were assigned to characteristic protons of heterocyclic or aromatic moieties. In the ^{1}H NMR spectra, the peaks of aromatic protons of resulting compounds were observed at 8.42–6.92 ppm, aliphatic protons appear in the region of 4.40–3.05 ppm, while methyl protons from the acetyl group in compound **3c** appeared at 1.89–182 ppm. A multiplet of a proton of the alkene group appeared in the region of 8.42–8.35 ppm. A splitting of these signals indicates that isolated compounds **3a**, **3b**, and **3c** containing several stereogenic centers were obtained as mixtures of diastereomers which could not be separated by purification procedures. The IR spectra are also characterized by the occurrence of two carbonyl absorptions at 1711 and 1661 cm^{-1}, and hydroxyl groups participating in hydrogen bonding give rise to a broad oscillation at 3620–3200 cm^{-1}.

Electron transitions to the higher energy states in **3a** and **3b** give two main absorption maxima at *ca.* 232 and 436 nm (Fig. 3). Since **3a** and **3b** contain several isolated π-electron systems, the total light absorption spectrum is a sum of the spectra of separate molecule fragments. The comparison of the UV/Vis spectra of compound **3a** with that of **3b** showed that compound **3a** gave an extra maximum at *ca.* 262 nm due to the lone pairs of sulfur atoms of the central linking fragment, i.e., 4,4′-thiobisbenzenethiol. The light absorption spectra of **3c** are identical to those of **3b** because of similar π-electron systems (Fig. 3).

TABLE 1 Glass Transition Temperature, Ionization Potential, and Electron Mobility of the Corresponding Compounds

Compound	T_g, °C	I_p, eV	μ, [cm^2/Vs] at the 10^6 V/cm electric field
3a	83	5.8	$2 \cdot 10^{-8}$
3b	74	5.85	$4 \cdot 10^{-8}$
3c	69	5.9	–

The existence of several diastereoisomers, the possibility of intermolecular hydrogen bonding and the flexibility of aliphatic linking chains make crystallization in the solid state difficult, so these materials are molecular glasses. The formation of the glassy state of **3a**, **3b**, and **3c** was confirmed by differential scanning calorimetric (DSC) analysis. The glass transition temperatures (T_g) of the investigated arylmetylene-1,3-indandione-based molecular glasses are presented in Table 1.

The results revealed that the obtained dimers exist only in the amorphous phase in our experiments. The glass transition temperatures of **3a** was observed at 83°C during the second heating, and no peaks due to crystallization and melting were observed (Fig. 1). The glass transition temperature of **3b** and its acylated analog **3c** was observed at 74 and 69°C, respectively. This means that the glassy state of the obtained materials is quite stable above room temperature. It is obvious that T_g of **3b** is lower than that of **3a** mainly due to the flexible

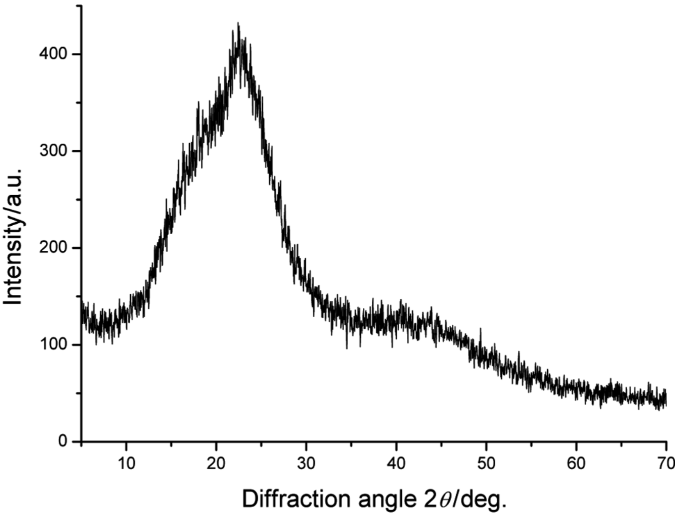


FIGURE 2 X-Ray diffraction patterns of **3a**.

linking fragments between chromophores. The replacement of hydroxyl groups with somewhat larger acyl moieties prevents the possible hydrogen bond formation and contributes to a decreased packing density of the molecules in **3c**. The amorphous state of **3a** was also confirmed by X-ray analysis (Fig. 2).

The glass-forming arylmethylene-1,3-indandiones **3a**, **3b**, and **3c** reported here are soluble in common organic solvents such as acetone, chloroform, THF, etc. Transparent films on substrates were prepared by the casting technique. The photoelectron emission spectra in air for the investigated molecular glasses are given in Figure 4, and the ionization potential (I_p) values are presented in Table 1. Due to the similar π-electron conjugation, as mentioned earlier, there is a small difference of the ionization potential values between **3a**, **3b**, and **3c**. These results indicate that the charge transport levels in the synthesized arylmethylene-1,3-indandione-based molecular glasses are energetically close.

Investigations of the electrochemical properties of the newly synthesized compounds **3b** and **3c** were also undertaken in this study. Cyclic voltammetry measurements on drop-cast films were conducted in acetonitrile with tetrabutylammonium perchlorate as the electrolyte. As an example, the cyclic voltammogram of a thin film of compound **3b** is shown in Figure 5.

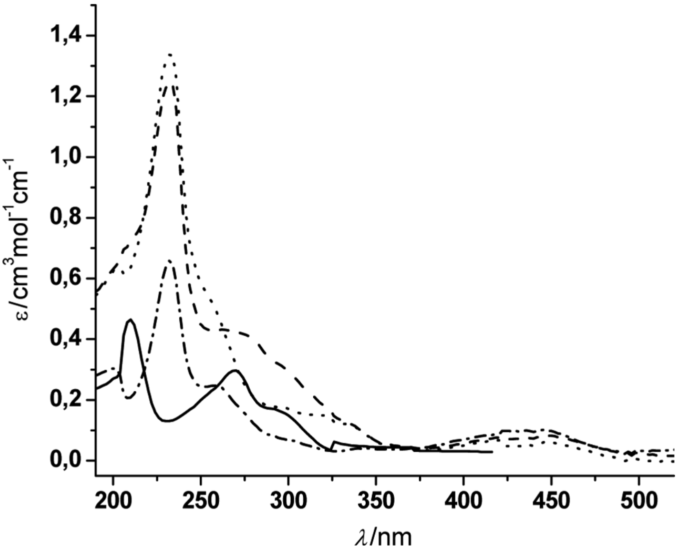


FIGURE 3 Absorption spectra of dilute THF solutions (10^{-4} M) of **2** (— · —), **3a** (– –), **3b** (. . .), and 4,4′-thiobisbenzenethiol (—).

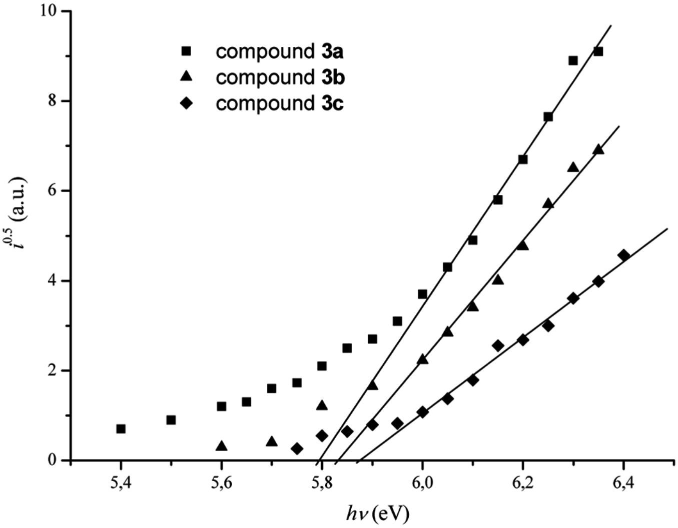


FIGURE 4 Photocmission (in air) spectra of compounds **3a**, **3b**, and **3c**.

It shows an electrochemically reversible reduction process occurring at $E_{1/2} = 1.02\,\text{V}$. However, the oxidation potentials were not observed clearly in CV measurements. The LUMO levels (vs vacuum) of compounds **3b** and **3c** are 3.9 and 3.6 eV, respectively. They were

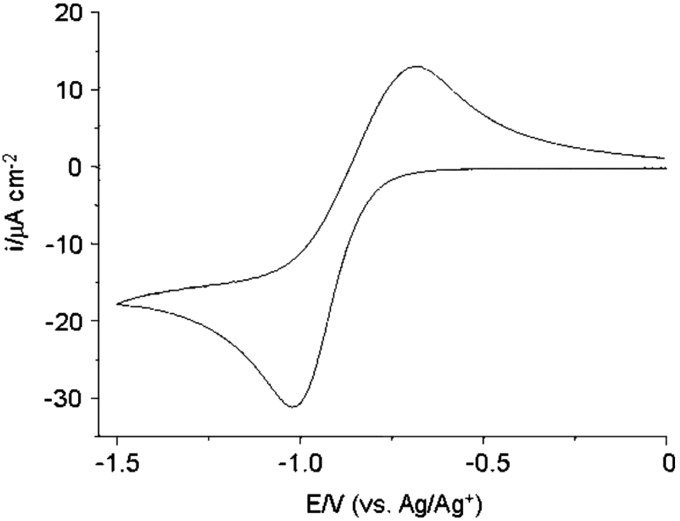


FIGURE 5 Cyclic voltammetry curve of a thin film of compound **3b**.

estimated from the onset of their reduction in cyclic voltammetry (on the basis that ferrocene/ferrocenium is by 4.8 eV below the vacuum level [21]). The calculated LUMO levels are close to *n*-type semiconductors used in solar cells [22]. In addition, the charge carrier mobility was measured by the time-of-flight technique. The electron drift mobility μ in **3a** and **3b** exceeds $10^{-8}\,\mathrm{cm^2V^{-1}s^{-1}}$ at the 10^6 V/cm electric field (Table 1).

CONCLUSIONS

In conclusion, three novel glass-forming arylmethylene-1,3-indandione derivatives **3a**, **3b**, and **3c** were synthesized. The molecular structure of these molecular glasses prevents the crystallization in a layer and allows stable films to be prepared even without polymeric binder. The ionization potentials of these molecular glasses are 5.8–5.9 eV. The electron mobility of **3a**, **3b**, and **3c** measured by the time-of-flight technique exceeds $10^{-8}\,\mathrm{cm^2V^{-1}s^{-1}}$ at strong electric fields. The LUMO levels (vs vacuum) of compounds **3b** and **3c** are 3.9 and 3.6 eV, respectively.

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