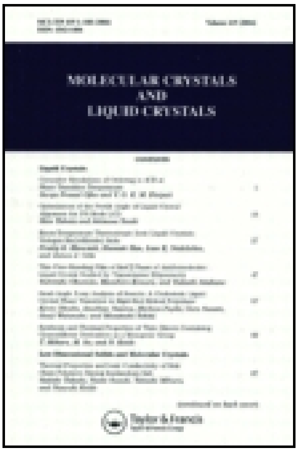

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Ramunas Lygaitis [a] , Juozas Vidas Grazulevicius [a] , Violeta Vaitkeviciene [b] & Vygintas Jankauskas [c]

[a] Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania

[b] Nuclear Engineering Laboratory, Lithuanian Energy Institute, Kaunas, Lithuania

[c] Department of Solid State Electronics, Vilnius University, Vilnius, Lithuania

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Electroactive Twin Compounds Containing Trioxothioxanthene Electron Accepting Moieties

RAMUNAS LYGAITIS,[1] JUOZAS VIDAS GRAZULEVICIUS,[1] VIOLETA VAITKEVICIENE,[2] AND VYGINTAS JANKAUSKAS[3]

[1]Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania
[2]Nuclear Engineering Laboratory, Lithuanian Energy Institute, Kaunas, Lithuania
[3]Department of Solid State Electronics, Vilnius University, Vilnius, Lithuania

Three dimeric molecules based on trioxothioxanthene and benzotriazole moieties were synthesized by alkylation and esterification reactions. The chemical structures of the compounds were confirmed by ^{1}HNMR, IR spectroscopies and mass spectrometry. Dilute solutions of trioxothioxanthene and benzotriazole-based compounds in THF absorb electromagnetic radiation in the region of 230–320 nm. 1,10-Bis-(9,10,10-trioxothioxanthen-3-yl-carboxy)decane can be transformed into the glassy state with the glass transition temperature of 35° C. It is capable of transporting negative charges. Electron drift mobility in the layers of trioxothioxanthene-based twin compound molecularly dispersed in PC-Z approaches 10^{-6} cm^2/Vs at an electric field of 1×10^6 V/cm.

Keywords Dimers; electron transport; trioxothioxanthene

Introduction

In contrast to numerous organic hole transport materials much less investigations have been done on organic electron–transporting materials [1]. One of the reasons for the lack of n-type semiconductors is the problem related to trapping. Since oxygen, a potential electron trap, is inevitably present, the reduction potential of the acceptor part of the molecule must be lower than that of oxygen. Therefore, stable under ambient conditions n-type semiconductors is of big interest. Previously we have reported on the synthesis and properties of bipolar molecules containing both electron acceptor and donor moieties. We have studied the charge and energy transport in the dilute solutions of one of 6-(9H-carbazole)hexyl 9,10,10-trioxo-9H-thioxanthen-3-oate [2,3]. In this work, we report on the synthesis and properties of

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Address correspondence to Juozas Vidas Grazulevicius, Department of Organic Technology, Kaunas University of Technology, Radvilenu Plentas 19, LT-3028, Kaunas, Lithuania. E-mail: Juozas.Grazulevicius@ktu.lt

potential electron–transporting compounds containing electronically isolated trioxothioxanthene and benzotriazole units. Trioxothioxanthene moiety is widely used in the synthesis of organic electron–transporting compounds, especially those designed for electrophotographic photoreceptors [4] and photorefractive materials [5,6]. Benzotriazole derivatives are also known as electron transporting materials [7].

Experimental

Materials

9,10,10-Trioxo-9H-3-thioxanthenecarboxylic acid, 1,6-dibromhexane, 1-H-benzotriazole, 1,10-decandiol, 4-dimethylaminopyridine, dicyclohexylcarbodiimide were purchased from "Aldrich". 9-H-carbazole, potassium fluoride were purchased from "Reakhim" (Russia). All chemicals were used as received without further purification.

1,6-Bis-(9,10,10-trioxothioxanthen-3-yl-carboxy)hexane (1)

To a magnetically stirred solution of 1.04 g (4.55 mmol) of 9,10,10-trioxo-3-thioxanthenecarboxylic acid in DMF 0.208 g (3.6 mmol) of potassium fluoride was added. Then 0.208 g (3.6 mmol) of 1,6-dibromhexane was added dropwise to the reaction mixture. The reaction mixture was heated at 90°C for 24 h and, after cooling down to the room temperature it was poured into water. Stable suspension was formed and it was destroyed by adding $Al_2(SO_4)_3$. The precipitated product was re-crystallized from DMSO and washed with diethyl ether. Yield: 0.203 g (44.3%) of white crystals (m.p.: 233°C, FW = 658 g/mol). ^1H NMR (250 MHz, $CDCl_3$, δ, ppm) 7.95 – 8.6 (m, 14H, ar), 4.4 (t, 4H, $2OCH_2$), 1.45–1.6 (m, 4H, $2CH_2$), 1.75–1.95 (m, 4H, $2CH_2$). An infrared absorption spectrum yielded the following peaks (KBr windows), (in cm^{-1}): ν (arene C–H) 3100; ν (aliphatic CH) 2950; ν (esteric C=O) 1720; ν (carbonylic C=O) 1680; ν (C=C in Ar) 1580; ν (SO_2) 1300, 1280, 1060; γ (C–H in Ar) 950. MS (70 eV): m/z = 658 (M^+), 289, 271.

1,10-Bis-(9,10,10-trioxothioxanthen-3-yl-carboxy)decane (2)

6.2 g (21.5 mmol) of 9,10,10-trioxo-3-thioxanthenecarboxylic acid, 1.5 g (8.6 mmol) of 1,10-decandiol, and 0.21 g (1.72 mmol) of 4-dimethylaminopyridine, and 250 ml of dry tetrahydrofuran were added into 250 ml flask fitted with a magnetic stirrer and a nitrogen inlet. The solution obtained was cooled down to 0°C and 3.91 g (18.9 mmol) of dicyclohexylcarbodiimide was added over 20 min. After 1 h of stirring the reaction vessel was allowed to warm up to the room temperature, and stirring was continued for an additional 48 hours to complete the reaction. The byproduct dicyclohexylurea was removed by filtration. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, chloroform) followed by recrystallization from the mixture acetone/chloroform. Yield: 1.9 g (29%) of white crystals (m.p.: 185–186°C, FW = 714 g/mol). A ^1H NMR spectrum yielded the following chemical shifts (300 MHz, $CDCl_3$, δ, ppm): 8.802 (d, 2H, $J = 0.9$ Hz, Ar), 8.406 (d, 4H, $J = 0.9$ Hz, Ar), 8.357 (dd, 2H, $J = 7.5$ Hz, $J = 1.5$ Hz, Ar), 8.205 (dd, 2H, $J = 7.5$ Hz, $J = 0.9$ Hz, Ar), 7.915 (dt, 2H, $J = 7.5$ Hz, $J = 1.5$ Hz, Ar), 7.82 (dt, 2H, $J = 6.6$ Hz), 4.41 (t, 4H, $J = 6.6$ Hz, OCH_2), 1.81 (p, 4H, OCH_2CH_2), 1.55–1.3 (m, 12H, $6CH_2$). An infrared absorption spectrum yielded the following peaks

(KBr window), (in cm^{-1}): ν (arene C–H) 3092; ν (aliphatic CH) 2926, 2860; ν (esteric C=O) 1723; ν (carbonylic C=O) 1681; ν (C=C in Ar) 1590, 1575; ν (SO_2) 1305, 1280; γ (C–H in Ar) 764, 750. MS ($APCI^+$, 20 V), m/z: 715 ($[M+H]^+$).

1-Bromo-6-(1-benzotriazolyl)hexane (3)

1.7 g (14.2 mmol) of benzotriazole and 0.97 g (2.8 mmol) of tetrabutylamoniumhydrosulphate were dissolved in 1,6-dibromhexane. 1.75 g (31.4 mmol) of potassium hydroxide was added stepwise and the reaction mixture was heated at 80°C for 12 h. The unreacted potassium hydroxide and inorganic salts were removed from the reaction mixture by filtration. 1,6-Dibromhexane was evaporated under vacuum. The resulting mixture was purified by aluminum oxide (II) column chromatography (ethyl acetate / n-hexane = 1:3) to yield 0.83 g (20.7%) of viscous liquid. A ^1H NMR spectrum yielded the following chemical shifts (100 MHz, $CDCl_3$, δ, ppm): 7.7–8.0 (m, 2H, ar), 7.22–7.55 (m, 2H, ar), 4.72 (t, 2H, $J = 8$ Hz, NCH_2), 3.36 (t, 2H, $J = 8$ Hz, $BrCH_2$), 2.12 (m, 2H, NCH_2CH_2), 1.84 (m, 2H, $BrCH_2CH_2$), 1.2–1.68 (m, 4H, $2CH_2$).

6-(Benzotriazol-1-yl)hexyl 9,10,10-trioxothioxanthen-3-oate (4)

To a magnetically stirred solution of 0.9 g (3.29 mmol) of 9,10,10-trioxo-3-thioxanthenecarboxylic acid in DMF 0.42 g (7.24 mmol) of potassium fluoride was added. Then 0.83 g (3.29 mmol) of 1-Bromo-6-(1-benzotriazolyl)hexane (**3**) was added to the reaction mixture. The reaction mixture was heated at 90°C for 4 h and, after cooling to the room temperature the precipitated product was filtered and washed with water and methanol. The resulting crystals were dried under vacuum. Yield: 0.6 g (37%) of white crystals (m.p.: 152°C, FW = 489 g/mol). A ^1H NMR spectrum yielded the following chemical shifts (300 MHz, $CDCl_3$, δ, ppm): 8.79 (s, 1H, ar), 8.43 (s, 1H, ar), 8.35 (d, 1H, $J = 7.5$ Hz, ar), 8.21 (d, 1H, $J = 7.75$ Hz, ar), 7.78–7.97 (m, 4H, ar), 7.33–7.42 (m, 2H, ar), 4.76 (t, 2H, $J = 6.87$ Hz, NCH_2), 4.39 (t, 2H, $J = 6.62$ Hz, OCH_2), 2.18 (p, 2H, NCH_2CH_2), 1.82 (p, 2H, $-OCH_2CH_2$), 1.26–1.63 (m, 4H, $2CH_2$). An infrared absorption spectrum yielded the following peaks (KBr windows), (in cm^{-1}): ν (arene C–H) 3100; ν (aliphatic CH) 2935, 2860; ν (esteric C=O) 1720; ν (carbonylic C=O) 1670; ν (C=C in Ar) 1590; ν (SO_2) 1300, 1280; ν (C–N) 1220; ν (SO_2) 1170, 1140; γ (C–H in Ar) 750. MS (70 eV): m/z = 489(M^+), 202, 146.

Methods

^1H NMR spectra were obtained on a Bruker AC 250 (250 MHz) instrument. Mass (MS) spectra were obtained on a Waters ZQ (Waters, Milford, USA). IR-spectroscopy was performed on Specord 75 IR and Perkin Elmer Spectrum GX spectrophotometers, using KBr pellets. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 20 instrument, equipped with low temperature probe. Thermogravimetric analysis (TGA) was fulfilled using NETZSCH STA 409 thermogravimeter, at 10°C/min heating rate under N_2 atmosphere. UV-VIS spectra were recorded with Spectronic Unicam Genesys^{TM} 8 spectrophotometer. Fluorescence emission spectra were recorded with a Hitachi MPF-4 luminescence spectrometer. Electron drift mobilities were measured by a xerographic time-of-flight method [8].

Results and Discussion

Synthesis and Characterization

The key step of the synthesis of compounds **1** and **2** is esterification reaction in DMF as a solvent in the presence of KF. This method was chosen due to several reasons. First of all 9,10,10-trioxo-3-thioxanthenecarboxylic acid has poor solubility in common organic solvents but it exhibits good solubility in hot DMF. On the other hand, this method offers rather simple synthetic route and good yields [9]. It is known that this reaction proceeds through the formation of hydrogen bond between the fluoride and the aromatic molecule, which directs electrons from the electron–rich fluoride anion to the organic part of the complex [10]. The nucleophilicity of the fluoride is much reduced by this H-bond formation, while at the same time the nucleophilicity of the hydroxyl oxygen is greatly increased. Using alkyl halides as the esterification reagents, various esters are easily prepared.

Compound **1** was synthesized using 1,6-dibromhexane in the presence of potassium fluoride and DMF as solvent at 90°C as shown in Scheme 1. The yield with the reaction time of 24 hours was 44.3%.

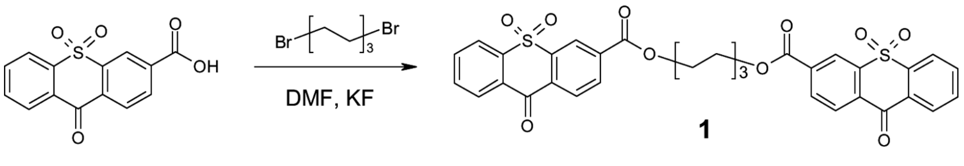
Twin molecule **2** containing 9,10,10-trioxothioxanthene units was prepared by esterification reaction of 9,10,10-trioxothioxanthene 3-carboxylic acid with 1,10-decandiol in the presence of 4-dimethylamino pyridine and dicyclohexylcarbodiimide as shown in Scheme 2.

Trioxothioxanthene and benzotriazole–based compound **4** was synthesized by the synthetic route, shown in Scheme 3. The first step was alkylation of benzotriazole with 1,6-dibromhexane using potassium hydroxide in the presence of tetrabutylammonium hydrogen sulphate as a phase transfer catalyst. The second step was esterification of 9,10,10-trioxo-9H-3-thioxanthenecarboxylic acid using 1-bromo-6-(1-benzotriazolyl)hexane (**3**) in the presence of potassium fluoride in DMF. The reactions was controlled by TLC and proceeded until the starting bromides were reacted fully. The yield of **4** was 37%.

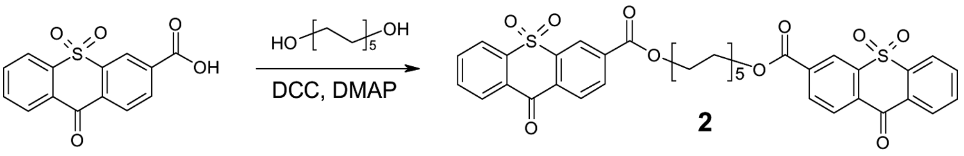
The synthesized compounds are soluble in common organic solvents such as chloroform, acetone, THF except twin compound **2**, which is soluble only in such solvents as DMF and DMSO. The chemical structures of the newly synthesized compounds **1, 2** and **4** were confirmed by ^{1}H NMR, IR spectroscopies and mass spectrometry.

Thermal Properties

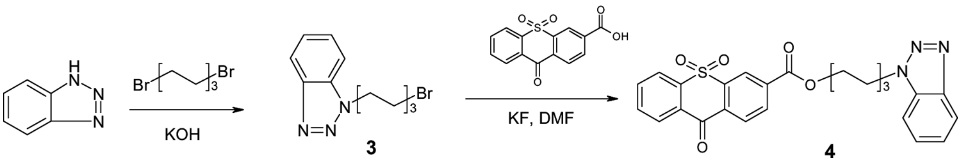
The thermal investigations of compounds **1, 2, 4** were performed by TGA and DSC. The transition temperatures are summarized in Table 1. The crystalline sample of **1** obtained by recrystallization from DMSO melted at 231°C and upon cooling only crystallization peak was observed at 176°C. In contrast, compound **2** showed the



Scheme 1. Synthesis of twin molecule **1**.



Scheme 2. Synthesis of twin molecule **2**.



Scheme 3. Synthesis of twin molecule **4**.

glass transition phenomenon and exhibited the polymorphism, taking on three different crystal forms. The first DSC heating run of this compound has revealed melting signal with the maximum at 178°C and no any peaks under cooling. When the sample was again heated, a glass–transition phenomenon was observed at 35°C, and then an exothermic peak due to crystallization was observed around 105°C. Thereafter, exothermic peaks due to solid–solid phase transitions from one crystal form to another were observed around 144°C, 160°C and 180°C respectively (Figure 1). Compound **4** showed not only glass transition ($T_g = 13°C$), but also crystallization at 92°C and melting at 151°C in the second heating cycle of DSC. It is evident that the twin compounds (**1, 2, 4**) containing trioxothioxanthene unit are more inclined to crystallization than the other twin compounds reported previously [2].

TGA has revealed relatively high thermal stability of the synthesized compounds. They exhibited an onset of degradation at temperatures higher than 300°C.

Optical and Photoelectrical Properties

Dilute solutions of trioxothioxanthene and benzotriazole-based compounds **1, 2, 4** in THF absorb electromagnetic radiation in the region of 230 – 320 nm. The absorption spectrum of compound **4** resembles the sum of the spectra of trioxothioxanthene and benzotriazole. Figure 2 shows fluorescence spectra of the dilute solutions of

Table 1. Thermal properties of compounds **1, 2, 4**

Compound	T_g, [°C]1)	T_m, [°C]1)	T_{cr}, [°C]1)	T_{ID}, [°C]2)
1	—	231	176	325
2	35	178	105	311a)
4	13	152	92	310

1)Determined by DSC, scan rate 10°C/min, N_2 atmosphere.

2)Onset of decomposition determined by TGA, heating rate 10°C/min, N_2 atmosphere.

a)Sublimation was observed.

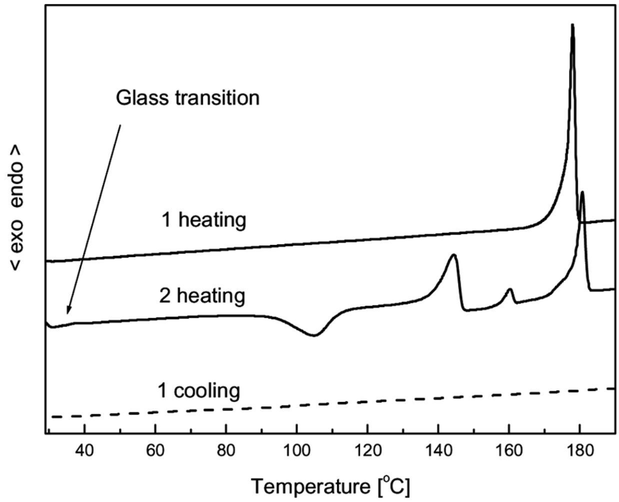


Figure 1. DSC thermogram of **2** (scan rate 10°C/min, N_2 atmosphere).

compounds **1** and **4**. These compounds emit in pure UV region. The fluorescence spectrum of **4** is red shifted by 13 nm with respect of the spectrum of **1**. The difference appears due to benzotriazole chromophore, which influences the alignment of the vibrational ground states.

Figure 3 shows the electric field dependence of the electron drift mobility of the 50% solid solution of trioxothioxanthene twin compound **2** in (PC-Z). The linear dependence of the electron drift mobility on the square root of the electric field was observed. The zero field electron drift mobility μ_0 of the twin compound **2** molecularly dispersed in PC-Z approaches $\sim 6 \cdot 10^{-10}\,\mathrm{cm^2/Vs}$ and at an electric field of 1×10^6 V/cm electron mobility approaches $10^{-7}\,\mathrm{cm^2/Vs}$.

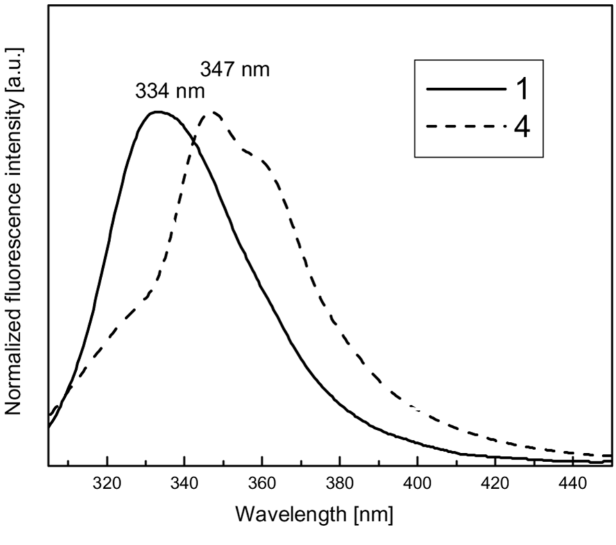


Figure 2. Fluorescence spectra of dilute THF solutions of compounds **1** ($\lambda_{ex} = 270$ nm), **4** ($\lambda_{ex} = 255$ nm), concentration of all solutions 10^{-6} M.

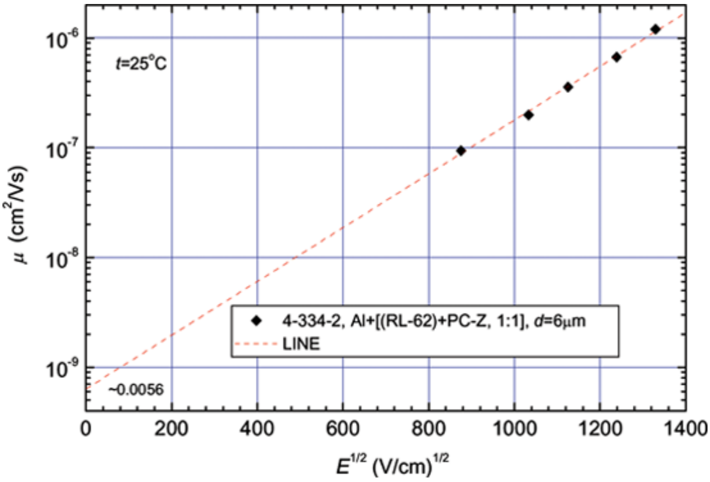


Figure 3. Electric field dependence of the electron drift mobility of the solid solution in PC-Z of twin compound **2**.

Investigations described above showed, that 9,10,10-trioxo-3-thioxanthenecarboxylic acid could be employed as electroactive chromophore for the synthesis of efficient n-type semiconductors and such materials could be used as electron transport materials in electrophotography or other organic optoelectronics devices.

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