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Octafluorobiphenyl-4,4′-diyl 9-oxothioxanthene-1,4-diyl polyether – a promising material for organic film based memristors: synthesis, memristive effect and charge transport mechanism

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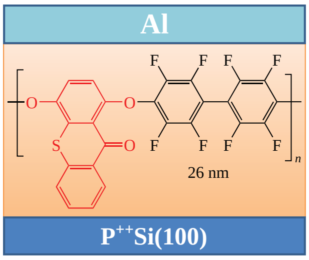
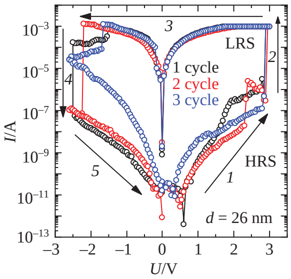
Polycondensation of perfluorobiphenyl with 1,4-dihydroxythioxanthen-9-one resulted in the title highly thermally stable polyether containing the thioxanthenone-type electron acceptor in-chain blocks in its structure. Model resistive memory devices based on it as the active medium exhibited a bipolar switching memristive effect with a 4-order difference in resistance between the low and high resistance states. The charge transport in this polyether is quantitatively described by the Nasyrov–Gritsenko model of phonon-assisted electron tunneling between traps.





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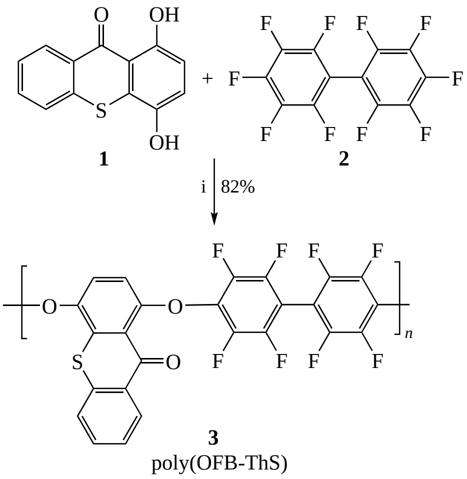
For the past 20 years, organic ambipolar polymers have been considered as promising materials for applications in organic electronics, including the fabrication of solar cells[1,2] and resistive memory devices. The latter application involves the use of polymers as active layers in metal–insulator–metal (MIM) or metal–insulator–semiconductor (MIS) structures, which can lead to the fabrication of low-cost, flexible, and three-dimensional devices.[3] Compared to inorganic dielectrics, the advantage of organic polymers as active working layers of memristors is due to their good film-forming ability, compatibility with metal and semiconductor platforms, structural flexibility, relative ease of fabrication of three-dimensional crossbar arrays, and sufficient thermal stability.[4–6] A large number of organic polymer types have been tested as active layers of the resistive memories,[7] but only a fraction of them have shown reliable memristive (reversible ON/OFF switching) behavior.[8–12]

Thioxanthone (9*H*-thioxanthen-9-one) and its derivatives are known as electrochemically active electron acceptor compounds[13] and have found a number of practical applications, including organic electronics.[14] MIS-type memory devices based on the ambipolar polyimides with thioxanthenone pendant groups[15] have demonstrated WORM (write-once-read-many-times) non-volatile behavior.[16] Methyl methacrylate copolymer with the same type of pendant groups was the first example of an organic polymer, in which the nature of the electron traps was confirmed by two independent experimental methods such as electrophysics and spectroelectrochemistry.[17]

1,4-Positioned CH fragments of the 9*H*-thioxanthen-9-one ring can be replaced by carbonyl groups using cyclization of arylsulfanylbenzoic acids obtained by the reaction of thiosalicylic acid with benzoquinone or other quinones.[18] This leads to the equilibrium mixture of the corresponding thioxanthenetriones[19] and 1,4-dihydroxy-1*H*-thioxanten-9-ones of type **1** (Scheme 1). The latter compounds have been shown to be electrochemically active electron acceptors.[19] The presence of two OH groups in the structures **1** motivated us to synthesize polyether **3** with octafluorobiphenyl-4,4′-diyl and 9-oxothioxanthene-1,4-diylbis(oxy) units, abbreviated as poly(OFB-ThS), which contains thioxanthone-like structures as an in-chain block. We also tested it for the use as an active layer in polymer-based memristors. Perfluorobiphenyl **2** (see Scheme 1) was chosen as the second



1 **2**

3
poly(OFB-ThS)

Scheme 1 *Reagents and conditions*: i, **1** (1.148 mmol), **2** (1.148 mmol), *N*,*N*-dimethylacetamide (DMAc), K_2CO_3 (2.296 mmol), 110 °C, 5 h.

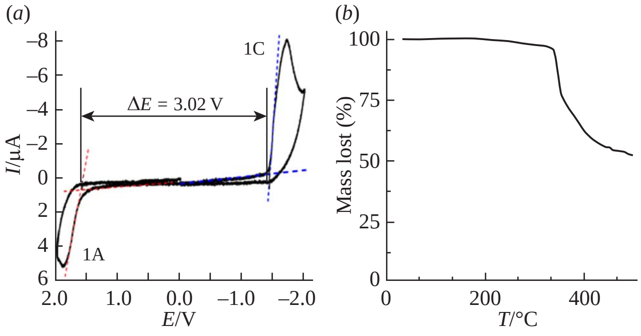


Figure 1 (*a*) Thin-layer cyclic voltammograms and (*b*) thermogravimetric curve in He atmosphere of poly(OFB-ThS) **3**. On part (*a*), 1C and 1A indicate the corresponding peaks, $E^{\mathrm{RED}}_{\mathrm{onset}}$, $E^{\mathrm{OX}}_{\mathrm{onset}}$ which are the onset reduction/oxidation potentials, the method for their determination is indicated by lines.

monomer for the polycondensation because this compound has two well-reacting 4,4′-positioned fluorine atoms thus providing good regioselectivity and the absence of branching in the polymer structure. Meanwhile, the presence of two F atoms in *ortho* positions of the benzene rings in final polymer **3** could lead to a decrease of the π-conjugation between thioxanthenone and tetrafluorobiphenyl fragments of the polymer chain, thus increasing the energy gap E_g of the polymer and avoiding its semiconductor properties.

Poly(OFB-ThS) **3** was synthesized by polycondensation of compounds **1** and **2** by their heating in DMAc in the presence of K_2CO_3 (see Scheme 1). The polymer **3** is characterized by high number-averaged (M_n = 7.1 kDa) and weight-averaged (M_w = 24.0 kDa) molecular weights. Its polydispersity index (M_w/M_n = 3.36) is good enough for thin film formation on Si and ITO wafers by centrifugation from the polymer solution. Polymer **3** is characterized by high thermal stability [Figure 1(*b*)] and also shows electrochemical reductive and oxidative activities. The thin film cyclic voltammograms (CVs) of polymer **3** showed irreversible reduction and oxidation peaks [Figure 1(*a*)], the corresponding peak and onset reduction/oxidation potentials being $E^{1C}/E^{\mathrm{RED}}_{\mathrm{onset}} = -1.71/-1.41$; $E^{1A}/E^{\mathrm{OX}}_{\mathrm{onset}} = -1.90/-1.58$. Using the peak onset potentials, the energy of the corresponding band gap E_g was estimated to be 3.02 eV, allowing the identification of polymer **3** as a dielectric, which is the main requirement for active layers of resistive memory devices to observe memristive effects.

The model memory devices of p^{++}Si(100)/**3**/Al and ITO/**3**/Al types were fabricated by centrifugation followed by thermal spraying of an upper Al electrode array through a shadow mask. The p^{++}Si(100)/**3**/Al memory device exhibited reversible resistive switching from the high resistance state (HRS) of the device to its low resistance state (LRS) when the voltage sweep changed from 0 to +3 V and back from LRS to HRS when the voltage sweep changed from 0 to –2.5 V [Figure 2(*a*)]. The memory window (the difference between HRS and LRS) is of four orders of magnitude which is satisfactory for practical applications in memristor technologies. The ITO/**3**/Al memory device also showed a bipolar switching memristive effect and is also characterized by a high memory window [Figure 2(*b*)].

The possibility of practical application of the polymer **3** film as the active medium of a memristor is demonstrated by the example of the p^{++}-Si based memory device [see Figure 2(*a*)]. This structure with a polymer film thickness of 26 nm exhibited reversible resistive switching from the high resistance state (HRS) to the low resistance state (LRS) and *vice versa* at rather low switching voltages (HRS → LRS ~ +3 V, LRS → HRS ~ –2.0 to –2.5 V). Due to these characteristics, the poly(OFB-ThS)-based memristor is a very low consumption memory device and can find a practical application in Resistive Random Access Memory (ReRAM) technology, because ReRAM technology requires a switching voltage of less than ± 5 V.

The study of charge transport mechanisms (leakage currents) can lead to the determination of the nature of electron traps in polymer films using experimentally obtained trap energy values. This can provide a better understanding of the mechanism of memristive switching. The time-of-flight transient experiments in polymers give the logarithmic mobility proportional to the square root of the electric field ($\sqrt{F}$).[20] Formally, such dependence is described by the Frenkel law.[21,22] To study the charge transport in the poly(OFB-ThS) film, a Si(100)/**3**/Al (d = 110 nm) structure was prepared, and its voltammetric characteristics in HRS were measured and simulated using the classical Frenkel approach and the Nasyrov–Gritsenko (NG) model of phonon-assisted tunneling between neighboring traps, which is used in the case of high trap concentration.[23]

The charge transport mechanism in a dielectric with traps is given by the expression[22]:

$$j = \frac{e}{a^2}P = eN^{2/3}P, \qquad (1)$$

where j is the current density through the MIS/MIM structure with a dielectric, e is the electron charge, a is an average distance between traps, $N = a^{-3}$ is the trap concentration and P is the trap ionization probability. The correct application of a charge transport model is thus reduced to an adequate description of P.

The use of the Frenkel model failed to describe the charge transport in the poly(OFB-ThS) film, because this model showed an immeasurably low electron trap concentration value, $N = 1.5 \times 10^{11}$ cm^{-3}.

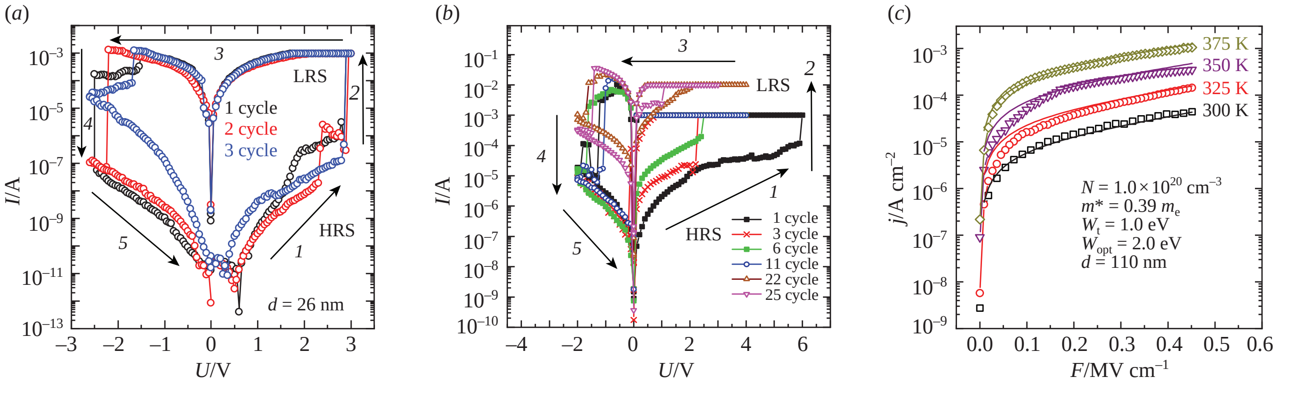


Figure 2 Bipolar switching memristive effects on the model memory devices fabricated using Si (p^{++} type) and ITO wafers: (*a*) p^{++}Si(100)/**3**/Al, (*b*) ITO/**3**/Al and (*c*) voltammetric (in j–F coordinates) characteristics of the Si(100)/**3**/Al device (film thickness d = 110 nm) at different temperatures (indicated by color) together with their simulations with the Nasyrov–Gritsenko model (experiment – symbols, simulation – solid curves).

In the NG model of charge transport, the electron tunneling from the trap to the neighboring trap takes place instead of that to the conduction band of the polymer due to the small distance between the traps.[23] The trap ionization probability in the NG model is described by the expression:

$$P = \frac{2\sqrt{\pi}\,\hbar W_\mathrm{t}}{m^* a^2 \sqrt{2kT(W_\mathrm{opt} - W_\mathrm{t})}} \exp\left(-\frac{W_\mathrm{opt} - W_\mathrm{t}}{kT}\right) \times \times \exp\left(-\frac{2a\sqrt{2m^* W_\mathrm{t}}}{\hbar}\right) \sinh\left(\frac{eFa}{2kT}\right), \qquad (2)$$

where $\hbar$ is the reduced Planck constant, W_t is the thermal ionization energy of the trap, m^* is the effective mass of electron and W_opt is the optical ionization energy of the trap.[17,23]

Since P value depends exponentially on a, [expression (2)] and, in turn, $a = N^{-1/3}$, it is possible to determine N from curve slope of the j–F characteristic [Figure 2(*c*)]. The corresponding simulation gives $N = 1.0\times10^{20}$ cm^{-3}, thermal trap ionization energy $W_\mathrm{t} = 1.0$ eV, optical trap ionization energy $W_\mathrm{opt} = 2.0$ eV and effective electron mass $m^* = 0.39\,m_\mathrm{e}$. The value of N obtained is satisfactory for the polymeric materials. Note that it may not correspond to the average concentration of in-chain electron acceptor blocks of the polymer, since the exact number of blocks involved in charge transport is unknown.

In conclusion, we have described the synthesis and properties of a novel electroactive polyaryl polyether, poly(OFB-ThS) **3**, with an electron-withdrawing thioxanthenone in-chain block and a polyfluoroaromatic tetrafluorobiphenyl fragment, which has been used for the first time in the design of organic polymers for ReRAM technologies. The memristor structure based on this polyether has shown a low switching voltages and a HRS to LRS ratio of four orders of magnitude, which is promising for its use as an active medium in memristors. The charge transport mechanism in the thin film of **3** was shown to be adequately described by the Nasyrov–Gritsenko model of phonon-assisted tunneling between electron traps rather than the classical Frenkel approach, because the latter model predicts an anomalously high value of the high-frequency permittivity and an anomalously low trap concentration.

To the best of our knowledge, poly(OFB-ThS) **3** is the first example of an ambipolar polymeric material with a perfluoroaryl in-chain block in its structure that has demonstrated a memristive effect with a high memory window. Thus, the use of polyfluoroaromatics as in-chain blocks may be a promising direction in the elaboration of ambipolar organic polymers for memristor technologies.

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Online Supplementary Materials

Supplementary data associated with this article (synthesis, NMR spectra, TG analysis, molecular weight, electrochemical and ellipsometric methods, fabrication of MIS/MIM structures and description of charge transport with the Frenkel model) can be found in the online version at doi: 10.1016/j.mencom.2024.09.013.

References

1 A. V. Lolaeva, A. N. Zhivchikova, M. M. Tepliakova, M. V. Gapanovich, E. O. Perepelitsina, A. F. Akhkiamova, D. A. Ivanov, N. A. Slesarenko, A. G. Nasibulin, A. V. Akkuratov and I. E. Kuznetsov, *Mendeleev Commun*., 2023, **33**, 682.

2 I. E. Kuznetsov, M. E. Sideltsev, V. G. Kurbatov, M. V. Klyuev and A. V. Akkuratov, *Mendeleev Commun*., 2022, **32**, 527.

3 L. Yuan, S. Liu, W. Chen, F. Fan and G. Liu, *Adv. Electron. Mater.*, 2021, **7**, 2100432.

4 Q.-D. Ling, D.-J. Liaw, C. Zhu, D. S.-H. Chan, E.-T. Kang and K.-G. Neoh, *Prog. Polym. Sci*., 2008, **33**, 917.

5 W.-P. Lin, S.-J. Liu, T. Gong, Q. Zhao and W. Huang, *Adv. Mater*., 2014, **26**, 570.

6 A. J. J. M. van Breemen, J.-L. van der Steen, G. van Heck, R. Wang, V. Khikhlovskyi, M. Kemerink and G. H. Gelinck, *Appl. Phys. Express*, 2014, **7**, 031602.

7 H.-J. Yen, C. Shan, L. Wang, P. Xu, M. Zhou and H.-L. Wang, *Polymers*, 2017, **9**, 25.

8 J. Zhao, L. Peng, Y.-L. Zhu, A.-M. Zheng and Y.-Z. Shen, *Polym. Chem*., 2016, **7**, 1765.

9 Y. Li, R. Fang, S. Ding and Y. Shen, *Macromol. Chem. Phys.*, 2011, **212**, 2360.

10 J. Jeong, M. J. Kim, W. S. Hwang and B. J. Cho, *Adv. Electron. Mater.*, 2021, **7**, 2100375.

11 B. H. Lee, H. Bae, H. Seong, D.-I. Lee, H. Park, Y. J. Choi, S.-G. Im, S. O. Kim and Y.-K. Choi, *ACS Nano*, 2015, **9**, 7306.

12 A. A. Minnekhanov, A. V. Emelyanov, D. A. Lapkin, K. E. Nikiruy, B. S. Shvetsov, A. A. Nesmelov, V. V. Rylkov, V. A. Demin and V. V. Erokhin, *Sci. Rep*., 2019, **9**, 10800.

13 N. V. Vasilieva, I. G. Irtegova, V. A. Loskutov and L. A. Shundrin, *Mendeleev Commun*., 2012, **22**, 111.

14 Y. Wang, Y. Zhu, G. Xie, Q. Xue, C. Tao, Y. Le, H. Zhan and Y. Cheng, *Org. Electron*., 2018, **59**, 406.

15 D. S. Odintsov, I. K. Shundrina, I. A. Os’kina, I. V. Oleynik, J. Beckmann and L. A. Shundrin, *Polym. Chem.*, 2020, **11**, 2243.

16 D. S. Odintsov, I. K. Shundrina, A. A. Gismatulin, I. A. Azarov, R. V. Andreev, V. A. Gritsenko and L. A. Shundrin, *J. Struct. Chem*., 2022, **63**, 1811.

17 A. A. Gismatulin, D. S. Odintsov, I. K. Shundrina, I. A. Os’kina, I. A. Azarov, L. A. Shundrin and V. A. Gritsenko, *Chem. Phys. Lett*., 2024, **810**, 141140.

18 V. A. Loskutov and I. V. Beregovaya, *Russ. J. Org. Chem*., 2009, **45,** 1405.

19 D. S. Odintsov, I. A. Os’kina, I. G. Irtegova and L. A. Shundrin, *Eur. J. Org. Chem.*, 2023, e202300459.

20 S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris and A. V. Vannikov, *Phys. Rev. Lett.*, 1998, **81**, 4472.

21 J. Frenkel, *Phys. Rev*., 1938, **54**, 647.

22 V. A. Gritsenko, T. V. Perevalov, V. A. Voronkovskii, A. A. Gismatulin, V. N. Kruchinin, V. Sh. Aliev, V. A. Pustovarov, I. P. Prosvirin and Y. Roizin, *ACS Appl. Mater. Interfaces*, 2018, **10**, 3769.

23 K. A. Nasyrov and V. A. Gritsenko, *J. Appl. Phys*., 2011, **109**, 093705.

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