

Proceeding Paper

Synthesis of C₆₀ Fullerene Hexakis Adducts Based on Strained Polycyclic Hydrocarbons and Their Application in Organic Electronics [†]

Arslan R. Akhmetov ^{1,*}, Rishat I. Aminov ¹, Zarema R. Sadretdinova ¹, Renat B. Salikhov ²,
Ilnur N. Mullagaliev ² and Timur R. Salikhov ²

¹ Institute of Petrochemistry and Catalysis of RAS, 450075 Ufa, Russia; rishaminov@gmail.com (R.I.A.); zarema.hairullina18@yandex.ru (Z.R.S.)

² Department of Infocommunication Technologies and Nanoelectronics, Ufa University of Science and Technology, 450075 Ufa, Russia; salikhovrb@yandex.ru (R.B.S.); ilnur9409@mail.ru (I.N.M.); timur-salikhov@yandex.ru (T.R.S.)

* Correspondence: akhmetov_arslan@mail.ru

[†] Presented at the 27th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-27), 15–30 November 2023; Available online: <https://ecsoc-27.sciforum.net/>.

Abstract: Using the Bingel–Hirsch reaction, new hexakis methanofullerenes containing strained polycyclic hydrocarbons were synthesized. Organic field-effect transistors were manufactured based on the obtained compounds.

Keywords: [60]fullerene; strained polycyclic hydrocarbons; Bingel–Hirsch reaction; hexamethanofullerene

1. Introduction

One of the most popular and promising areas for the use of fullerene derivatives is the creation of organic field-effect transistors due to the covalent binding of fullerenes with electron-donating or photoactive macromolecules, which forms a molecular heterojunction [1].

The most selective method for the synthesis of hexakis methanofullerenes is the Bingel–Hirsch reaction [2,3], which makes it possible to obtain fullerene C₆₀ [4–6] hexaadducts with *Th*-symmetry [4] that can be used as n-type acceptor materials with a high charge carrier mobility and electrical stability [7–11]. The search for organic semiconductors for creating field-effect thin-film transistors is an urgent task. It is known from the literature [12,13] that manufactured organic field-effect transistors based on styrylfullerenes are significantly superior in efficiency to devices created on the basis of PCBM. Based on the above, it follows that C₆₀ fullerene derivatives are promising objects for creating organic systems that can act as n-type semiconductors.

2. Results and Discussion

Previously, we [14] were the first to synthesize hybrid molecules from C₆₀ fullerene and strained polycyclic hydrocarbons, on the basis of which organic field-effect transistors (OFETs) with high-quality films were created. In development of these studies, according to the well-known method [4], we carried out the selective synthesis of C₆₀ hexaadducts containing six SPH (strained polycyclic hydrocarbon) addends in order to increase the solubility of new hybrid molecules, as well as their promising direction associated with the creation of methanofullerenes, which are an effective n-type organic semiconductor, due to a larger number of covalently attached SPH groups to the C₆₀ carbon cage. Thus, using the reaction of nucleophilic addition to fullerene C₆₀ of α -halocarbanions generated in situ by the interaction of esters 1–3 with CBr₄ in the presence of the base 1,8-diazabicyclo



Citation: Akhmetov, A.R.; Aminov, R.I.; Sadretdinova, Z.R.; Salikhov, R.B.; Mullagaliev, I.N.; Salikhov, T.R. Synthesis of C₆₀ Fullerene Hexakis Adducts Based on Strained Polycyclic Hydrocarbons and Their Application in Organic Electronics. *Chem. Proc.* **2023**, *14*, 68. <https://doi.org/10.3390/ecsoc-27-16147>

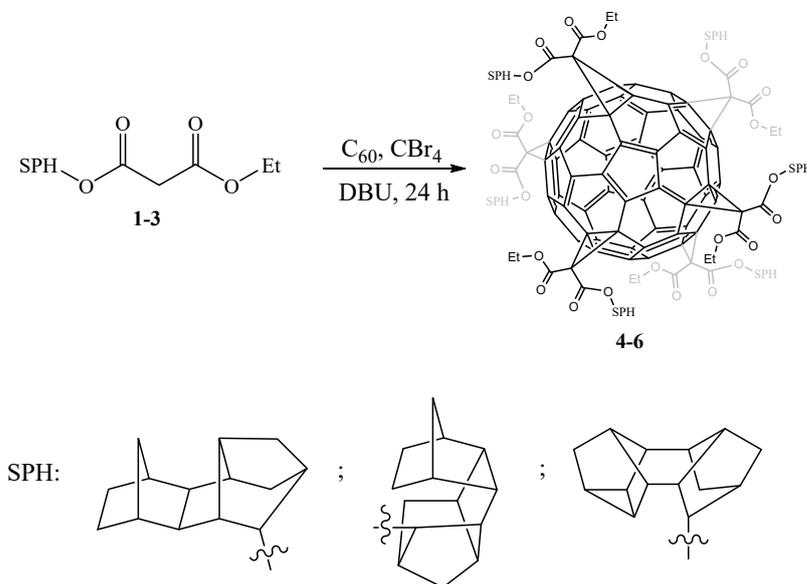
Academic Editor: Julio A. Seijas

Published: 15 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

[5.4.0]undec-7-ene (DBU) in the ratio 1:10:100:10, respectively, under the developed conditions (orthodichlorobenzene, 20 °C, 24 h) (Scheme 1), the target fullerene hexaadducts 4–6 were synthesized with a yield of ~96%.



SPH—strained polycyclic hydrocarbon

Scheme 1. Synthesis of hexakisadduct methanofullerenes.

To manufacture transistors, we used a method described earlier [14]; the structure of a field-effect transistor is shown in Figure 1. In a similar way, the current–voltage characteristics were measured and the mobility of charge carriers in the active layer of μ OFETs was calculated (Table 1).

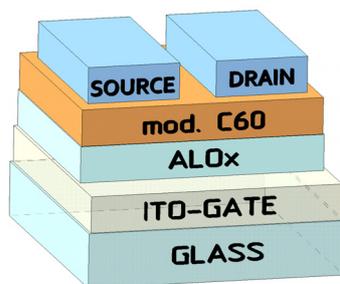


Figure 1. Structure of a field-effect transistor with films of fullerene derivatives.

Table 1. Charge carrier mobility values.

Sample	Mobility, cm ² /V·s
4	0.005
5	0.007
6	0.012

Current–voltage characteristics (Figures 2–4) were measured at room temperature without an inert atmosphere. Under the application of a positive gate voltage, the current exhibits an increase, indicating the prevalence of electronic conductivity in the transport channel of the OFETs. The dependences are non-linear, lacking saturation regions in the output characteristics of the devices. The absence of saturation sections in the output characteristics may be attributed to the existence of leakage currents.

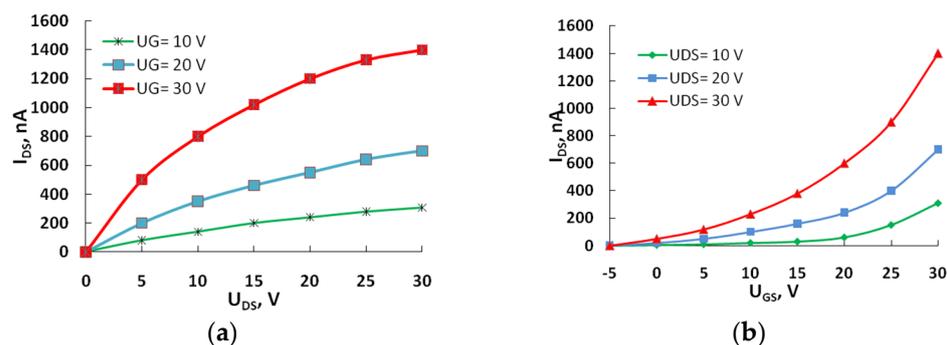


Figure 2. The output (a) and transfer characteristics (b) of the field-effect transistor with active layer 4.

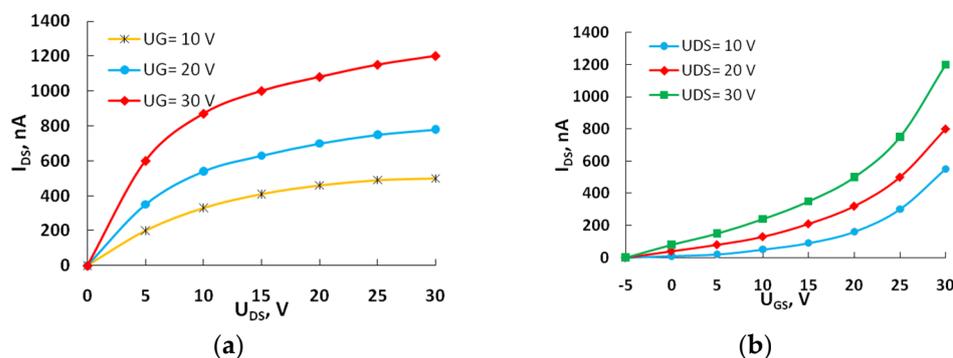


Figure 3. The output (a) and transfer characteristics (b) of the field-effect transistor with active layer 5.

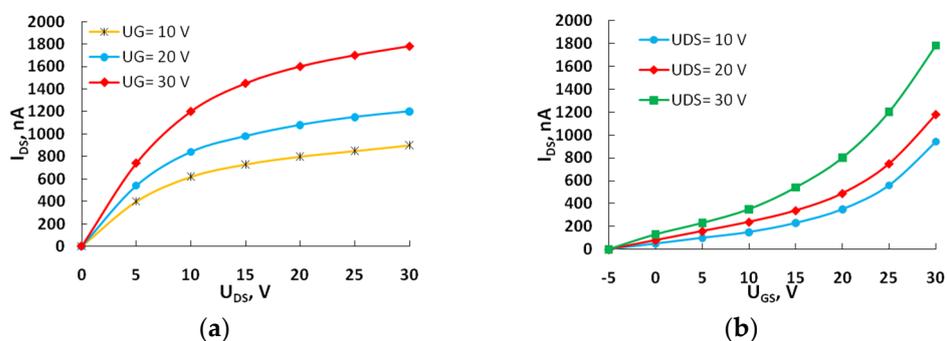


Figure 4. The output (a) and transfer characteristics (b) of the field-effect transistor with active layer 6.

Current–voltage characteristics were measured at room temperature without an inert atmosphere.

3. Materials and Methods

All reactions were performed under an argon atmosphere and in anhydrous solvent. The solvents and reagents were dried or refined according to the literature procedures. Commercially available [60]fullerene (99.5% pure, Sigma-Aldrich, 9402 Alberene Drive, Houston, TX, USA) was used. The reaction products were analyzed on an HPLC chromatograph Shimadzu SPD-20A (1900 SE 4th Avenue, Canby, OR, USA) equipped with a UV detector at 313 or 340 nm. The mixtures were separated on a preparative column Cosmosil Buckyprep Waters (250 × 10 mm) at ~20 °C. Toluene was used as an eluent; the flow rate was 3.0 mL·min⁻¹. The ¹H and ¹³C NMR spectra were procured on a Bruker Avance-500 spectrometer at 500.17 and 125.78 MHz, respectively. A mixture of CDCl₃ and CS₂ (1:5) was used as a solvent. The chemical shifts are reported as δ values in parts per million relative to the internal standard Me₄Si. The coupling constants (J) are reported in Hertz. The mass spectra were obtained on an UltraFlex III TOF/TOF (Bruker Daltonik GmbH, Karlsruhe, Germany) operating in linear (TOF) and reflection (TOF/TOF)

positive and negative ion modes. S₈ and DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) were used as the matrix. For the application on a metal target, toluene solutions of the samples were used.

For transistor creation, ITO-coated glass substrates were used. A 400 nm-thick AlOx film was spin-coated onto the ITO layer. Then, using the vacuum thermal evaporation method, aluminum electrodes with a thickness of 500 nm were deposited onto the AlOx dielectric layer. After this, fullerene derivatives with a thickness of 150 nm were deposited using the centrifugation method. To prepare a solution for centrifugation, 5 mg of the fullerene derivative and 200 µl of toluene were used. The size of the source and drain contacts with a gap of 2 mm between them was 4 mm. To carry out the process, an SM-6M centrifuge, a vacuum unit (VUP5), an HY3005D-3 direct current source, a GDM 8245 multimeter (microammeter), an AFM Nanoeducator II and Gwyddion software (<http://gwyddion.net/> accessed on 3 December 2023) were used. Fullerene derivatives 4–6 were synthesized using a known procedure [6].

3.1. Hexamethanofullerene 4

Brown powder. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 4.43–4.34 (m, 12H, CH₂), 2.55 (b, m, 12H, CH), 2.17–2.02 (m, 12H, CH), 1.97–1.93 (m, 12H, CH), 1.83–1.74 (m, 12H, CH), 1.61–1.55 (m, 12H, CH), 1.38–1.34 (m, 18H, 6CH₃), 1.13–1.07 (m, 12H, CH), 0.93–0.77 (m, 12H, CH). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 163.90, 163.35, 145.99, 145.54, 145.41, 141.29, 141.03, 140.99, 89.56, 69.11, 62.75, 57.63, 54.43, 53.89, 46.88, 43.57, 41.78, 39.45, 36.89, 36.00, 34.86, 29.36, 29.07, 14.14. MALDI TOF [M][−] calcd. for C₁₇₄H₁₄₄O₂₄ 2616.9981; Found 2616.9978. Yield 48 mg, 96%.

3.2. Hexamethanofullerene 5

Brown powder. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 4.41–4.35 (m, 12H, CH₂), 2.54 (b, m, 12H, CH), 2.28–2.24 (m, 12H, CH), 2.17–2.11 (m, 12H, CH), 2.05–1.99 (m, 12H, CH), 1.89–1.82 (m, 12H, CH), 1.46–1.43 (m, 12H, CH), 1.37–1.31 (m, 18H, 6CH₃), 0.92–0.84 (m, 12H, CH), 0.79–0.77 (m, 12H, CH). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 163.87, 163.40, 147.15, 145.57, 141.30, 140.92, 89.85, 69.11, 62.74, 54.59, 53.43, 50.64, 50.08, 46.87, 42.30, 41.87, 40.45, 38.98, 36.93, 36.41, 24.04, 14.12. MALDI TOF [M][−] calcd. for C₁₇₄H₁₄₄O₂₄ 2616.9981; Found 2616.9985. Yield 44 mg, 95%.

3.3. Hexamethanofullerene 6

Brown powder. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 4.99–4.90 (m, 12H, CH₂), 2.33–2.32 (m, 12H, CH), 2.31–2.30 (m, 12H, CH), 2.13–2.11 (m, 12H, CH), 2.05–1.95 (m, 12H, CH), 1.93–1.77 (m, 12H, CH), 1.66–1.63 (m, 12H, CH), 1.55–1.47 (m, 12H, CH), 1.36–1.32 (m, 18H, 6CH₃), 1.23–1.20 (m, 12H, CH), 1.02–0.98 (m, 12H, CH). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 163.67, 162.81, 147.19, 145.49, 141.48, 86.07, 84.25, 69.22, 52.42, 44.65, 42.94, 41.40, 40.06, 36.63, 35.66, 34.61, 33.64, 32.32, 30.12, 15.83, 14.95, 14.82. MALDI TOF [M][−] calcd. for C₁₇₄H₁₃₂O₂₄ 2604.9042; Found 2604.9039. Yield 46 mg, 95%.

4. Conclusions

The calculated charge carrier mobilities reflect the corresponding changes for pairs (a and b). Hybrid molecules of hexakis adducts of C₆₀ fullerene 4 and 6 contain six fragments of a strained polycyclic hydrocarbon; the best charge carrier mobility μ result for the device shown in Figure 1 was shown by methanofullerene 6, where $\mu = 0.012 \text{ cm}^2/\text{V}\cdot\text{s}$, and methanofullerenes 4 and 5, with $\mu = 0.005 \text{ cm}^2/\text{V}\cdot\text{s}$ and $\mu = 0.007 \text{ cm}^2/\text{V}\cdot\text{s}$, respectively. The manufactured organic field-effect transistors showed a high electrical stability; the current value remained the same during repeated measurements.

Author Contributions: Conceptualization, data curation, synthetic investigation, writing—original draft, review and editing, A.R.A., R.I.A., Z.R.S., R.B.S., I.N.M. and T.R.S.; supervision, R.B.S. All authors have read and agreed to the published version of the manuscript.

Funding: Fullerene derivatives were obtained in the framework of the Ministry of Science and Higher Education within the State assignment Institute of Petrochemistry and Catalysis of RAS State Registration FMRS-2022-0075, FMRS-2022-0076 and the research was funded with the support of a state assignment (scientific code FZWU-2023-0002).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: Structural studies were performed using the equipment of the Collective Usage Centre 'Agidel' at the Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Cravino, A.; Sariciftci, N.S. Double-cable polymers for fullerene based organic optoelectronic applications. *J. Mater. Chem.* **2002**, *7*, 1931–1943. [[CrossRef](#)]
2. Bingel, C. Cyclopropanierung von Fullerenen. *Chem. Berichte* **1993**, *126*, 1957–1959. [[CrossRef](#)]
3. Camps, X.; Hirsch, A. Efficient cyclopropanation of C₆₀ starting from malonates. *J. Chem. Soc. Perkin Trans. 1* **1997**, *11*, 1595–1596. [[CrossRef](#)]
4. Hirsch, A.; Vostrowsky, O. C₆₀ Hexakisadducts with an Octahedral Addition Pattern—A New Structure Motif in Organic Chemistry. *Eur. J. Org. Chem.* **2001**, *5*, 829–848. [[CrossRef](#)]
5. Yan, W.; Seifermann, S.M.; Pierrat, P.; Bräse, S. Synthesis of highly functionalized C₆₀ fullerene derivatives and their applications in material and life sciences. *Org. Biomol. Chem.* **2015**, *13*, 25–54. [[CrossRef](#)] [[PubMed](#)]
6. Lorenz, P.; Hirsch, A. Photoswitchable Norbornadiene–Quadricyclane Interconversion Mediated by Covalently Linked C₆₀. *Chem. Eur. J.* **2020**, *26*, 5220–5230. [[CrossRef](#)] [[PubMed](#)]
7. Tuktarov, A.R.; Salikhov, R.B.; Khuzin, A.A.; Popod'ko, N.R.; Safargalin, I.N.; Mullagaliev, I.N.; Dzhemilev, U.M. Photocontrolled organic field effect transistors based on the fullerene C₆₀ and spiropyran hybrid molecule. *RSC Adv.* **2019**, *9*, 7505–7508. [[CrossRef](#)] [[PubMed](#)]
8. Robin, M.; Harnois, M.; Molard, Y.; Jacques, E. Improvement of n-type OTFT electrical stability by gold electrode modification. *Org. Electr.* **2016**, *39*, 214–221. [[CrossRef](#)]
9. Zhou, K.; Dong, H.; Zhang, H.L.; Hu, W. High performance n-type and ambipolar small organic semiconductors for organic thin film transistors. *Phys. Chem. Chem. Phys.* **2014**, *16*, 22448–22457. [[CrossRef](#)] [[PubMed](#)]
10. Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting π -Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics. *Chem. Rev.* **2012**, *112*, 2208–2267. [[CrossRef](#)] [[PubMed](#)]
11. Sadretdinova, Z.R.; Akhmetov, A.R.; Salikhov, R.B.; Mullagaliev, I.N.; Salikhov, T.R. 1,2,3-Triazolylfullerene-based n-type semiconductor materials for organic field-effect transistors. *Mend. Comm.* **2023**, *33*, 320–322. [[CrossRef](#)]
12. Tuktarov, A.R.; Chobanov, N.M.; Budnikova, Y.H.; Dudkina, Y.B.; Dzhemilev, U.M. Synthesis and electrochemical properties of fullerenylnystyrenes. *J. Org. Chem.* **2019**, *84*, 16333–16337. [[CrossRef](#)] [[PubMed](#)]
13. Tuktarov, A.R.; Chobanov, N.M.; Sadretdinova, Z.R.; Salikhov, R.B.; Mullagaliev, I.N.; Salikhov, T.R.; Dzhemilev, U.M. New n-type semiconductor material based on styryl fullerene for organic field—Effect transistors. *Mendeleev Commun.* **2021**, *31*, 641–643. [[CrossRef](#)]
14. Akhmetov, A.R.; Aminov, R.I.; Mullagaliev, I.N.; Salikhov, R.B. Synthesis of hybrid molecules based on strained polycyclic hydrocarbons and fullerene C₆₀: Application of thin films based on them in organic electronics. *Russ. J. Gen. Chem.* **2023**, *9*, 1315–1325. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.