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Synthesis of C_{60} Fullerene Hexakis Adducts Based on Strained Polycyclic Hydrocarbons and Their Application in Organic Electronics [†]

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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-Hirsh reaction; hexamethanofullerene

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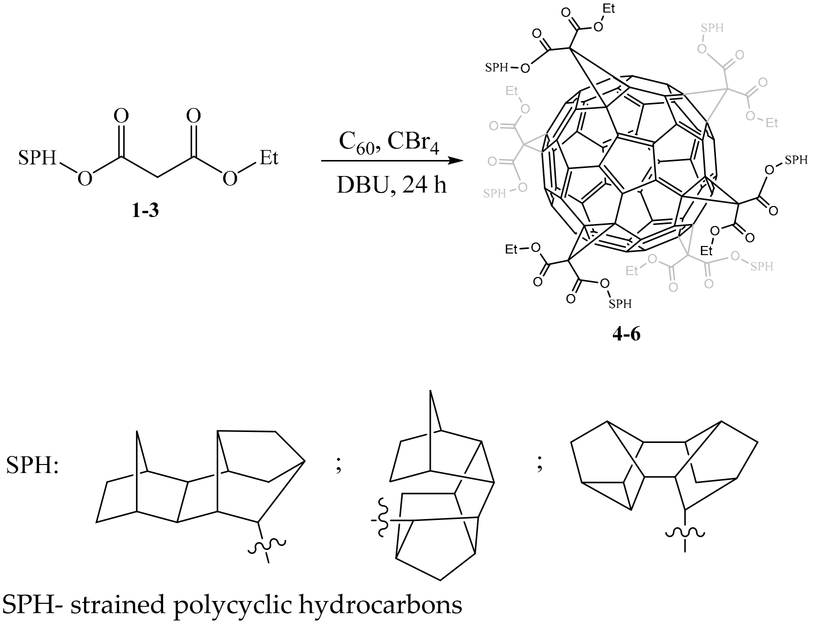
1. Introduction

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 C_{60} [4–6] hexaadducts with *Th*-symmetry [4] which can be used as n-type acceptor materials with 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 C_{60} 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 C_{60} 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 C_{60} 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 organic semiconductor n- type, due to a larger number of covalently attached SPH to the C_{60} carbon cage. Thus, using the reaction of nucleophilic addition to fullerene C_{60} of α-halocarbanions generated in situ by the interaction of esters **1–3** with CBr_4 in the presence of the base 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), taken 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%.



Scheme 1. Synthesis of hexakisadduct methanofullerenes containing functionally substituted strained polycyclic hydrocarbons.

To manufacture transistors, we used the 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).

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 increment, 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.

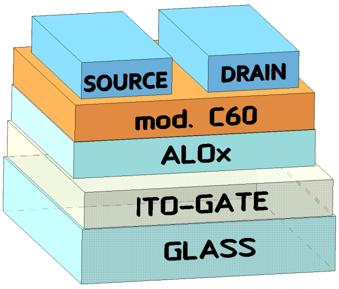
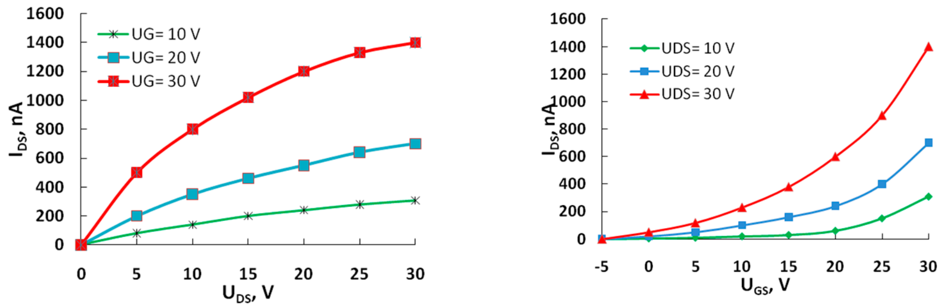


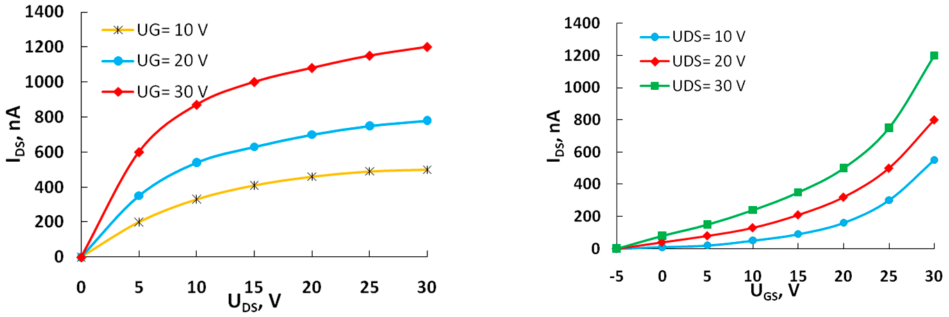
Figure 1. Structure of a field-effect transistor with films of fullerene derivatives.

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



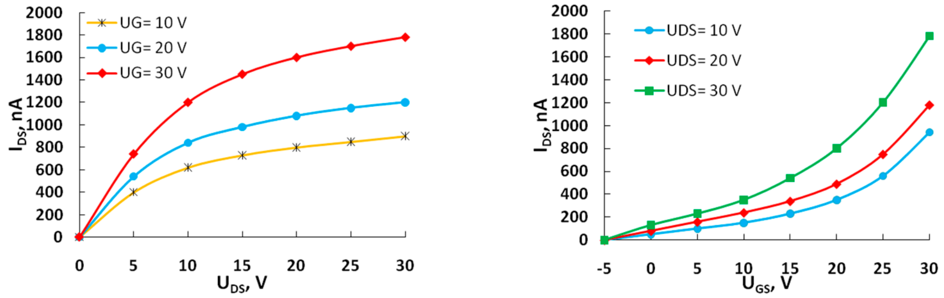
(**a**) (**b**)

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



(**a**) (**b**)

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



(**a**) (**b**)

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

Table 1. Charge carrier mobility values.

Sample	Mobility, $cm^2/V*s$
4	0.005
5	0.007
6	0.012

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) were used. The reaction products were analyzed on a HPLC chromatograph Shimadzu SPD-20A (Japan) equipped with the 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 eluent, the flow rate was 3.0 mL·min^{-1}. The ^{1}H and ^{13}C NMR spectra were run on a Bruker Avance-500 spectrometer at 500.17 and 125.78 MHz, respectively. A mixture of $CDCl_3$ and CS_2 (1:5) was used as a solvent. The chemical shifts are reported as δ values in parts per million relative to internal standard Me_4Si. The coupling constants (J) are reported in Hertz. The mass spectra were obtained on an UltraFlex III TOF/TOF (Bruker Daltonik GmbH, Germany) operating in linear (TOF) and reflection (TOF/TOF) positive and negative ion modes. S_8 and DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyliden]malononitrile) were used as the matrix. For the application on a metal target, toluene solutions of the samples were used. ITO-coated glass substrates were used for the manufacture of transistors. A 400 nm AlOx film was deposited on ITO by the spin coating technique. Aluminum films, source–drain contacts with a thickness of 500 nm, were deposited on the dielectric AlOx layer by the vacuum thermal evaporation technique. Then 150 nm thick films of fullerene derivatives were deposited by centrifugation. The spin coating solution was prepared from 5 mg of a fullerene derivative and 200 μL of toluene. The size of source–drain contact with a 2 mm gap was 4 mm. Centrifuge CM-6M, vacuum unit (VUP5), DC Power Supply HY3005D-3, multimeter GDM 8245 (microammeter), SPM Nanoeducator II, Gwyddion software. Fullerene derivatives **4**–**6** were synthesized according to a known procedure [6].

3.1. *Hexamethanofullerene* 4

Brown powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.43–4.34 (m, 12H, CH_2), 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, $6CH_3$), 1.13–1.07 (m, 12H, CH), 0.93–0.77 (m, 12H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{174}H_{144}O_{24}$ 2616.9981; Found 2616.9978. Yield 48 mg, 96%.

3.2. *Hexamethanofullerene* 5

Brown powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.41–4.35 (m, 12H, CH_2), 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, $6CH_3$), 0.92–0.84 (m, 12H, CH), 0.79–0.77 (m, 12H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{174}H_{144}O_{24}$ 2616.9981; Found 2616.9985. Yield 44 mg, 95%.

3.3. *Hexamethanofullerene* 6

Brown powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) =4.99–4.90 (m, 12H, CH_2), 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, $6CH_3$), 1.23–1.20 (m, 12H, CH), 1.02–0.98 (m, 12H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{174}H_{132}O_{24}$ 2604.9042; Found 2604.9039. Yield 46 mg, 95%.

4. Conclusions

Thus, the calculated charge carrier mobilities reflect the corresponding changes for pairs (a and b). Hybrid molecules of hexakis adducts of C_{60} fullerene **4** and **6** contain six fragments of a strained polycyclic hydrocarbon, the best result of charge carrier mobility μ in the device shown in Figure 1 was shown by methanofullerene **6** where μ = 0.012 cm^2/V·s, and **4** and **5** μ = 0.005 cm^2/V·s and μ = 0.007 cm^2/V·s, respectively. The manufactured organic field-effect transistors showed high electrical stability; the current value remained the same during repeated measurements.

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