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Compound based on star-shaped oligophenylene and fullerene C_{60}

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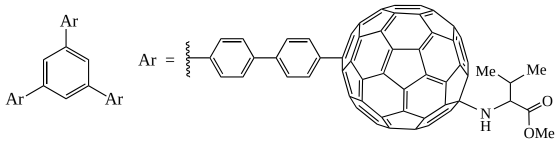
Compound based on star-shaped oligophenylene and modified with l-valine fullerene C_{60} has been synthesized and characterized. For characterization, X-ray photoelectron spectroscopy was used.



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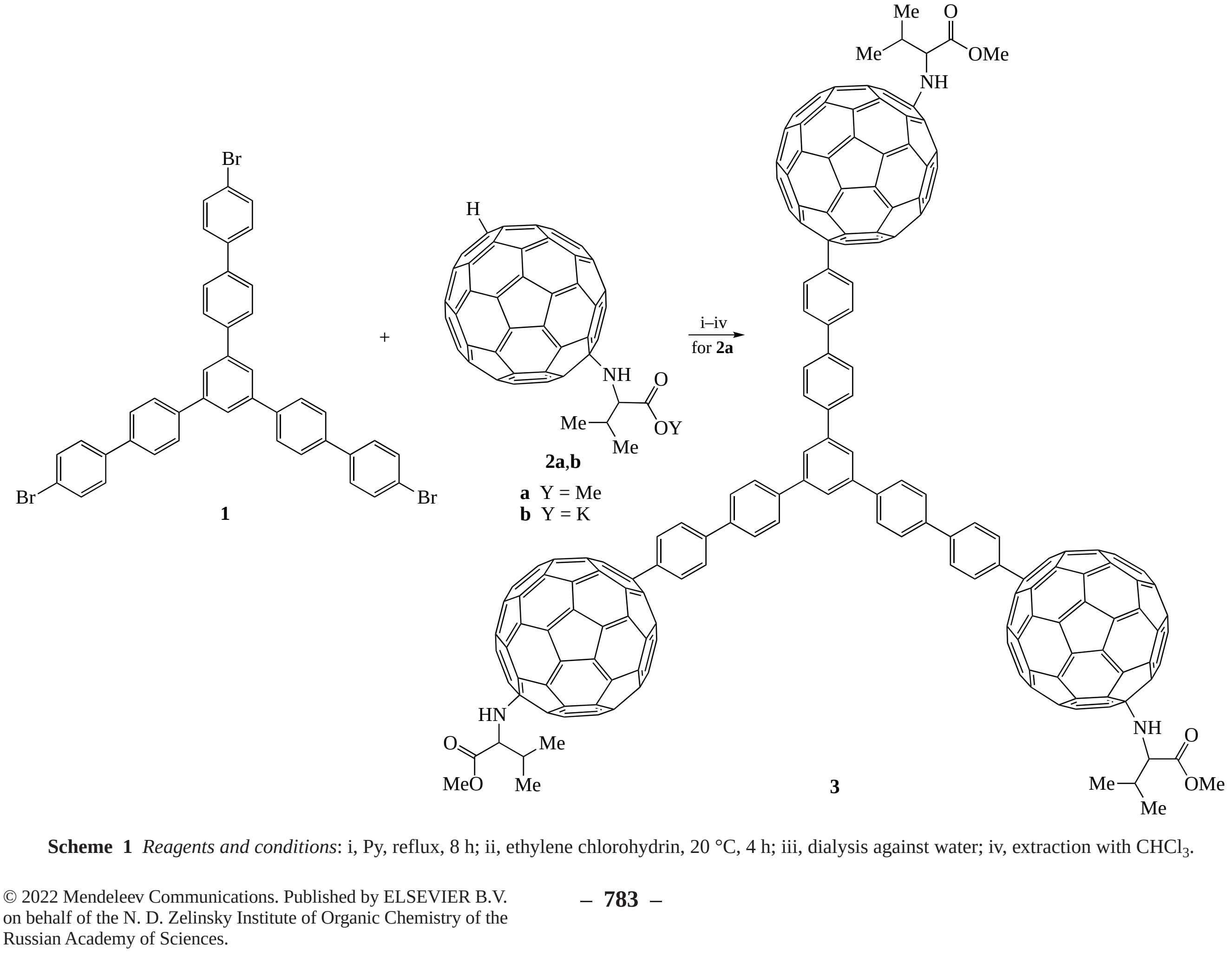
In recent decades, the huge consumption of hydrocarbons has led to an increase in carbon dioxide emissions into the air.[1] One way to reduce carbon dioxide emissions from industrial sources can be its absorption. The success of this process depends on the development of an optimal sorbent with high absorption capacity, good selectivity, fast kinetics, recycle stability, mechanical and chemical strength, and easy regeneration.[2–5] Microporous solid absorbers currently used to capture and separate CO_2 are based on activated carbon, carbon nanotubes, graphene-based materials, organic carbonized polymers, molecular sieves or zeolites.[6]

Branched polyphenylenes[7,8] obtained by cyclocondensation of acetylarenes after thermal structuring become excellent microporous carbon materials with a specific surface area up to 1000 $m^2\ g^{-1}$. They possess high strength, chemical and thermal stability, and therefore can be used as highly heat-resistant



Scheme 1 *Reagents and conditions*: i, Py, reflux, 8 h; ii, ethylene chlorohydrin, 20 °C, 4 h; iii, dialysis against water; iv, extraction with $CHCl_3$.

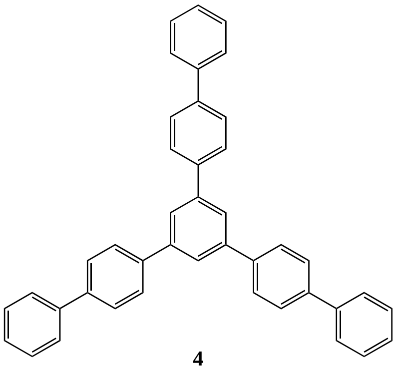
sorbents. On the other hand, fullerene C_{60} is known to improve the gas separation capacity of various materials.[9–11] Despite the polarization capability and high chemical activity, fullerene exhibits outstanding stability. For example, C_{60} sublimates without decomposition at 873 K.[12] Therefore, compounds comprising polyphenylene and fullerene structural units seem to be useful materials for absorbing and separating gases.[13,14]

In this work, the reaction of branched bromine-containing oligophenylene **1** with amino acid fullerene C_{60} derivative (AFD) **2a** was performed (Scheme 1). Oligophenylene **1** represents the structural element of branched polyphenylenes family.[8] Amino acid hydrofullerene derivatives usually couple with halogen-containing compounds easily[15] due to the presence of active hydrogen on the C_{60} framework. Amino acid hydrofullerenes during the reaction with bromides behave like ionic surfactants having a polar group whose charge is opposite in sign to that of the surface.

Compound **2a** was obtained according to the previously described method.[16,17] To prepare the target oligophenylene–fullerene conjugate, we used a tribromine-containing cyclotrimer **1**,[18] 1,3,4-tris(4′-bromobiphenyl-4-yl)benzene, obtained in turn by cyclocondensation of 4-(4-bromophenyl)-acetophenone. Bromine-containing oligophenylene **1** reacted with a monoamine derivative of fullerene, *N*-monohydro-fullerenyl-L-valine methyl ester **2a** to give product **3** (see Scheme 1). The reaction was carried out in pyridine since both the starting compound and the product were soluble in this solvent.

To separate the reaction product **3** from bromine-containing oligophenylene **1** and excess unreacted **2a**, ethylene chlorohydrin was injected into the reaction mixture[19] to convert **2a** into the water-soluble derivative while compound **3** was not water-soluble. Isolated compound **3** was soluble only in *N*-methylpyrrolidone.

The IR spectra of compound **3** and relative 1,3,5-tris(biphenyl-4-yl)benzene **4** representing the central fragment of compound **3** were compared[18] (see Online Supplementary Materials, Figure S2). The IR spectrum of **3** contains bands characteristic of elements of the aromatic structure (1074, 1385–1436, 1635 cm^{-1}), as well as bands characteristic of fullerene (537, 1179 cm^{-1}).[20] In addition, this spectrum contains a band at 1715 cm^{-1}, which apparently belongs to the amino acid carbonyl group.



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To confirm the structure of compound **3**, it would be desirable to take its NMR spectrum, unfortunately, it was not possible due to insolubility of **3** even in pyridine. It was also impossible to record an NMR spectrum of the precursor **2a** since solutions of AFDs were reported as colloidal systems with a high degree of association.[17,21,22] The association propensity of compound **3** in solution could be judged when its molecular weight was evaluated by GPC (in *N*-methylpyrrolidone). The analysis showed that M_w was 8260 while the calculated molecular weight was 3080. Ordinary elemental analysis also could not be performed, since under the analysis conditions the fullerene sublimated.[17]

Table 1 Elemental composition (at%) of the samples studied.

Sample	O	C	N	K
C_{60}	1.9	98.1		
4	0.6	99.4		
2b	20.2	74.7	1.5	3.7
3	15.9	81.8	2.3	

The best method to characterize compound **3** seemed to be X-ray photoelectron spectroscopy (XPS). For a comparative study, three reference samples, *viz*. compound **1**, potassium salt **2b** and cyclotrimer **4** were selected (Table 1).

Figure 1 shows the C1s spectra of fullerene C_{60}, **4**, **2b** and **3** samples fitted with some Gaussian peaks using the reliable chemical shifts.[23] The main peaks at ~284.8, 285.7, 286.5, 287.5 and 288.6 eV correspond to the C–C/C–H, C–N, C–OH and/or C–O–C, C=O and or O–C–O, and C(O)O groups, respectively. The spectra of fullerene C_{60} and **4** contain four shake-up satellite peaks related to aromaticity of the compounds. Taking into account the low intensities of shake-up satellites related to phenylenes and fullerenes and their overlap with peaks corresponding to certain groups, their isolation in the spectra of samples **2b** and **3** was not carried out.[23]

The binding energies (E_b), Gaussian widths (W), and relative intensities (I_{rel}) of photoelectron peaks belonging to different chemical groups in the C1s and N1s spectra are presented in Table S1 (see Online Supplementary Materials). It should be noted that the C=O and/or O–C–O groups are absent in the sample **2b**, which may be assigned to its oxidation during the synthesis and isolation. The relative intensities of C–O–C/C–OH groups in **2b** and **3** samples are evidenced on their excessive contents. Their excesses may be assigned to oxidation as well. The spectrum K2p, presented in Figure 1(*c*) is described by two $K2p_{3/2}$ and $K2p_{1/2}$ peaks at 293.1 and 295.9 eV with peak widths of 1.24 and 1.26 eV and a branching ratio of 2 : 1. Figure 2 shows the N1s spectra of the **2b** and **3** samples. The first spectrum is approximated with two Gaussian peaks at 398.8 and 399.7 eV with the same peak width of 0.88 eV. Their relative intensities are 0.58 and 0.42. The peak at 399.7 eV is assigned to C_{60}–NH bond, while the binding energy of 399.8 is close to that of pyridine (solvent in the synthesis). The second spectrum is fitted with three peaks at 399.2, 400.1 and 402.1 eV with peak widths

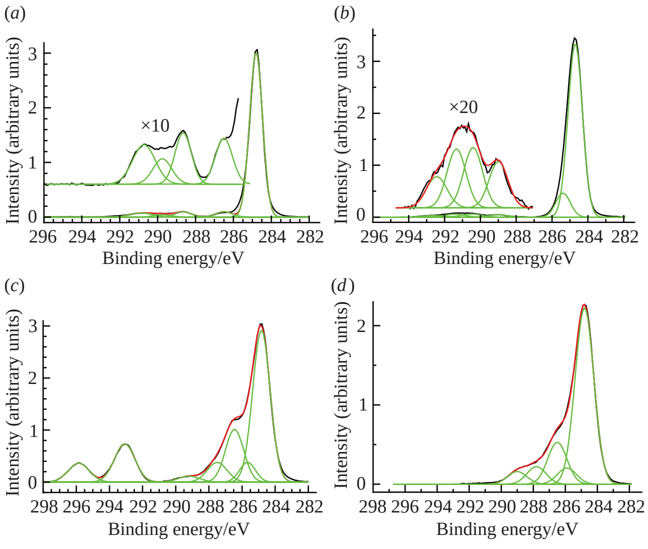

Figure 1 High-resolution C1s XPS spectra of (*a*) fullerene C_{60}, (*b*) compound **4**, (*c*) potassium salt of **2b** and (*d*) compound **3**.

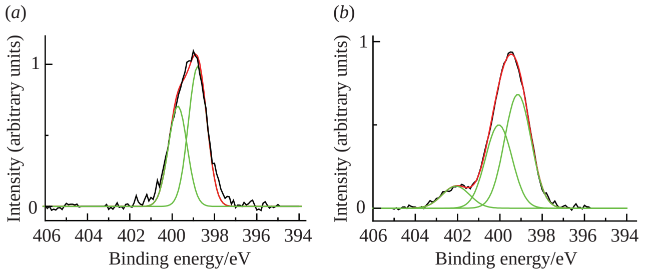

Figure 2 High-resolution N1s XPS spectra for (*a*) potassium salt **2b** and (*b*) compound **3**.

of 1.25, 1.25 and 1.3 eV, respectively, which may be assigned to aromatic N, C_{60}–NH bond and NH^{3+} group. Their relative intensities are 0.52, 0.38 and 0.1.

The given data for samples C_{60} and **4** shows their purity. The absence of bromine in sample **3** unambiguously confirms its formation. The presence of excess nitrogen in the sample may indicate the presence of a solvent (pyridine), in which the reaction was carried out. Pyridine could be captured during the formation of associates.[21,24] An excess oxygen content may indicate partial oxidation of fullerene during the isolation of the final product.

In conclusion, a reaction of an aromatic tribromide with an amino acid derivative of fullerene C_{60}, *N*-monohydrofullerenyl-L-valine methyl ester, was carried out. This open up the prospect of obtaining fullerene derivatives of polyphenylenes and using them for the targeted delivery of drugs or as CO_2 sorbents.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.11.025.

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