

Information and thermodynamic entropies of regioisomeric fullerene cycloadducts $C_{60}(CH_2)_n$ ($n = 1, 2$) and $C_{70}CH_2$

Alina Tukhbatullina¹, Aleksandr Turbin¹, and Denis Sabirov^{1,*}

¹Laboratory of Mathematical Chemistry, Institute of Petrochemistry and Catalysis UFRC RAS, 450075 Ufa, Russia

Abstract. The computations of the thermodynamic and information entropies of regioisomeric mono- and bisadducts of the C_{60} and C_{70} fullerenes with cyclopropane addends were performed with the density functional theory method. The regularities between the entropies and symmetry point groups of the molecules are discussed. For isomeric compounds, the calculated thermodynamic and information entropies vary in narrow ranges; the ranges for both entropies are narrower as compared with the ranges observed for these quantities of fullerenes themselves. The information entropy is recommended as a parameter for digital selecting the most and least symmetric structures.

1 Introduction

Currently, information entropy (h) is used as a structural descriptor. It is calculated based on partitioning the molecule's atoms over the atom types [1-10]. Such a partition indirectly accounts point symmetry groups of the molecules and the use of the h values allows digital recognizing less and more symmetric molecules in the considered series [11-14]. High-symmetry molecules are divided into large atomic types and, consequently, they have low information entropies [14], and *vice versa*. When considered structurally related chemical compounds (*e.g.*, isomers), it is possible to reveal the correlations between the thermodynamic (S°) and information entropies. For example, in the case of the isomers of the C_{60} fullerene, the S° and h values decrease with the symmetry point group [15]. A linear correlation was found between the ΔS°_R and Δh_R for the atomization of saturated hydrocarbons (including linear and branched alkanes and cycloalkanes) [16].

Previously, we studied the information entropy of the C_{60} -based nanostructures: oligomers $(C_{60})_n$ [17], dimers $(C_{60})_2$ [18] with different types of connecting units, and endofullerenes [14, 19]. The advantage of the C_{60} as a building block for structural design deals with the possibility of tuning the symmetry of the obtained nanostructures. Information-entropy indices in this regard can be used as structural descriptors for digital classification of the nanostructures and searching for structure—property relationships with different molecular and physicochemical parameters of chemical compounds [20, 21].

In the present work, we have studied the thermodynamic and information entropies of the regioisomeric bisadducts C_{60} and C_{70} with cyclopropane cycles annulated to the fullerene core. Compounds $C_{60/70}(CH_2)_n$ and their substituted derivatives make up a

widespread type of fullerene adducts, which are used in the organic chemistry of fullerenes and materials science [22-29].

2 Computation details

Thermodynamic and information entropies were calculated using the standard methods. The molecules of fullerene adducts were optimized with density functional theory method PBE/3 ζ [30] in program PRIRODA-11 [31]. Then we defined the symmetry point group of the molecule using program ChemCraft [32]. The rotation numbers (σ) corresponding to the found symmetry were used for the calculations of thermodynamic entropy (standard conditions, the PBE/3 ζ method). The chosen method reliably reproduces the known thermodynamic entropies of pristine fullerenes C_{60} and C_{70} . Their experimental entropies S° are 544.0 and 641.0 J mol⁻¹ K⁻¹, respectively [33]. The computed entropies are following, J mol⁻¹ K⁻¹: $S^\circ(C_{60}) = 548.5$ (symmetry I_h , $\sigma = 30$) and $S^\circ(C_{70}) = 616.2$ (symmetry D_{5h} , $\sigma = 10$). The fullerene structures are shown in Figure 1.

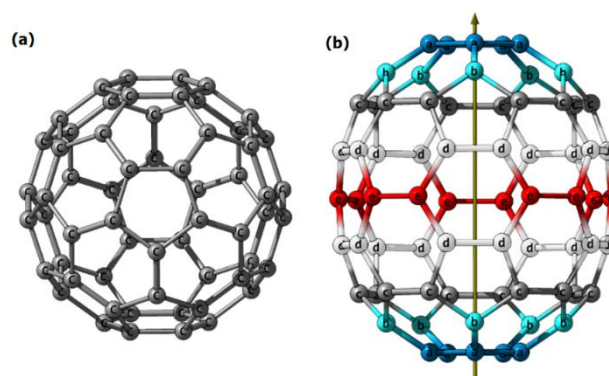


Fig. 1. Fullerenes C_{60} and C_{70} . Different colors correspond to the atoms belonging to different atom types.

* Corresponding author: diozno@mail.ru

The information entropies of the fullerene adducts were calculated using their molecular graphs (so-called Schlegel diagrams), in which the inequivalent vertices were colored. The information entropy of the N -atomic molecule was calculated as:

$$h = -\sum_{j=1}^n \frac{N_j}{N} \log_2 \frac{N_j}{N} \quad (1)$$

where n is the number of atom types in the molecule, and $\frac{N_j}{N}$ are their populations herewith $\sum_{j=1}^n \frac{N_j}{N} = 1$. In the sense of structural chemistry, the number of atom types n corresponds to the number of the peaks of ^{13}C NMR spectrum of the fullerene adduct (and their intensities are theoretically proportional to their population ratios).

3 Results and discussion

3.1 Thermodynamic and information entropies of the 6.6-closed and 5.6-open adducts C_{60}CH_2

C_{60}CH_2 , the simplest representative of the cyclopropafullerenes, has two structural isomers, in which the CH_2 addend is attached to 6.6 or 5.6 bond (according to the trivial fullerene nomenclature, 6.6 bond is a carbon—carbon bond common for two hexagons of the fullerene skeleton 5.6 bond is common for pentagon and hexagon). If CH_2 is added to the 5.6 bond, the bond is cleaved; in the case of the 6.6 addition, the bond remains as is. Therefore, these isomeric adducts C_{60}CH_2 are called 6.6-closed and 5.6-open [22, 24] (Figure 2).

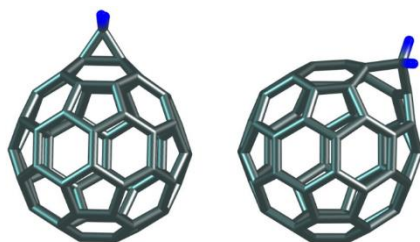


Fig. 2. Isomeric monoadducts C_{60}CH_2 : 6.6-closed (left) and 5.6-open (right).

The molecules of the 6.6-closed and 5.6-open adducts are characterized with the symmetry point groups C_{2v} and C_s and partitions over atom types $1 \times 1 + 5 \times 2 + 13 \times 4$ and $7 \times 1 + 28 \times 2$, respectively (the conventional partition formula implies [number of atom types] \times [number of atoms in the type]). The calculations *via* Equation (1) gives the following values: $h_{66} = 4.168$ и $h_{56} = 5.088$ bit/atom. The quantum-chemically calculated thermodynamic entropies are: $S_{66}^\circ = 589.0$ and $S_{56}^\circ = 595.5 \text{ J mol}^{-1} \text{ K}^{-1}$. Thus, lower h and S° values correspond to the isomer C_{60}CH_2 with C_{2v} symmetry, which is higher than the symmetry of its counterpart.

The 6.6-closed fullerene adducts are more stable as compared with their 5.6-open isomers though both can be

synthesized [22, 24]. Below, we consider only 6.6-functionalized fullerene adducts.

3.2 Thermodynamic and information entropies of the 6.6-closed bisadducts $\text{C}_{60}(\text{CH}_2)_2$

Fullerene bisadducts are also formed in the addition reactions to fullerenes. Regioisomerism (or positional isomerism) is inherent in this type of fullerene derivatives due to the different arrangement of the addends on the fullerene skeleton. In the case of symmetric addends CH_2 attached to the 6.6 bonds, eight positional isomers $\text{C}_{60}(\text{CH}_2)_2$ exist (Figure 3). The computed thermodynamic and information entropies are collected in Tables 1 and 2.

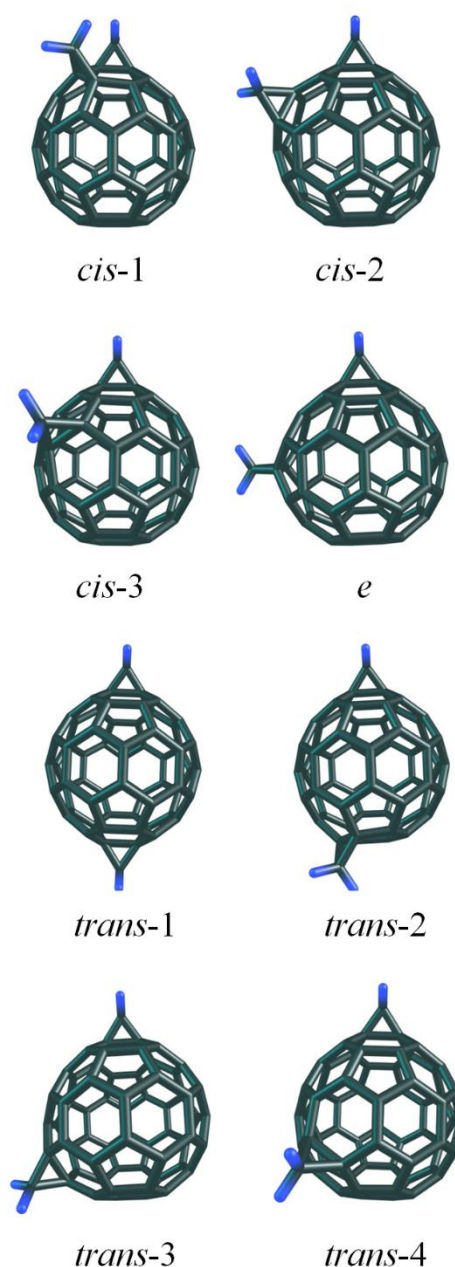


Fig. 3. Regioisomeric 6.6-closed bisadducts $\text{C}_{60}(\text{CH}_2)_2$

We note a symbatic behavior of the computed values of h and S° in the series of $C_{60}(CH_2)_2$ (Figure 4). Molecule $C_{60}(CH_2)_2$ -*trans*-1 demonstrate the lowest entropies here and it is also the most symmetric species in the series (it has D_{2h} symmetry).

Table 1. Thermodynamic entropy of the $C_{60}(CH_2)_2$ regioisomers ($J mol^{-1} K^{-1}$)

Isomer	Contributions to the total value*			S°_{tot}
	S_{trans}	S_{rot}	S_{vib}	
<i>cis</i> -1	191.4	158.2	260.4	610.1
<i>cis</i> -2	191.4	158.3	263.3	612.9
<i>cis</i> -3	191.4	152.5	265.4	609.3
<i>e</i>	191.4	158.3	262.8	612.5
<i>trans</i> -1	191.4	146.7	263.4	601.5
<i>trans</i> -2	191.4	152.5	263.5	607.4
<i>trans</i> -3	191.4	152.5	263.4	607.3
<i>trans</i> -4	191.4	152.5	263.3	607.2

* Hereinafter, S_{trans} , S_{rot} , and S_{vib} are the contributions to the thermodynamic entropy associated with the translational, rotational and vibrational motions of the molecule.

Table 2. Symmetry, partition and information entropy of the $C_{60}(CH_2)_2$ regioisomers

Regioisomer	Symmetry	σ	Partition over atom types	h (bit/atom)
<i>cis</i> -1	C_s	1	$4 \times 1 + 31 \times 2$	5.105
<i>cis</i> -2	C_s	1	$4 \times 1 + 31 \times 2$	5.105
<i>cis</i> -3	C_2	2	33×2	5.044
<i>e</i>	C_s	1	$8 \times 1 + 29 \times 2$	5.166
<i>trans</i> -1	D_{2h}	4	$1 \times 2 + 4 \times 4 + 6 \times 8$	3.347
<i>trans</i> -2	C_2	2	33×2	5.044
<i>trans</i> -3	C_2	2	33×2	5.044
<i>trans</i> -4	C_s	1	$4 \times 1 + 31 \times 2$	5.105

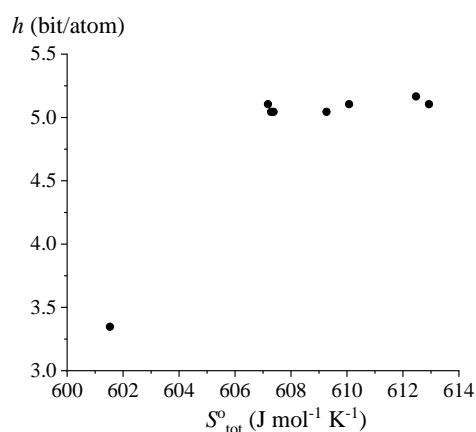


Fig. 4. Thermodynamic vs. information entropies of the 6.6-closed bisadducts $C_{60}(CH_2)_2$.

Isomers having the same symmetry are characterized with the same (in the case of C_2 symmetry) or close values (C_s symmetry) of information entropies. For the C_2 -symmetry isomers, the h values are the same due to their same partitions (Table 2). Most of C_s -isomers have $h = 5.105$ bit/atom except of e - $C_{60}(CH_2)_2$ with $h = 5.166$ bit/atom. This is due to the different partition of the last one. Indeed, the C_s symmetry implies only one symmetry element, *viz.* the symmetry plane that divides the molecule

over two equivalent parts. The atoms in these parts form doubly populated atom types. Other m atoms of the molecule lie in this plane and form singly populated atom types. The partition formula for all C_s -symmetry structures is $(N - m)/2 \times 2 + m \times 1$. Thus, the information entropy of the C_s -symmetric molecules depends on m : for the *cis*-1, *cis*-2 and *trans*-4 isomers, $m = 4$ whereas $m = 8$ in the case of e - $C_{60}(CH_2)_2$.

3.3 Thermodynamic and information entropies of 6.6-monoadducts $C_{70}CH_2$

There are 8 types of atoms in the C_{70} (D_{5h}) molecule (Figure 1). They are trivially designated with the first Latin letters. The atoms form 4 types of the 6.6 bonds: *ab*, *cc*, *de*, and *ee*. We have considered all the corresponding isomers (Figure 5) though it is known that the addition reactions proceed preferably *via ab* and *cc* bonds [34].

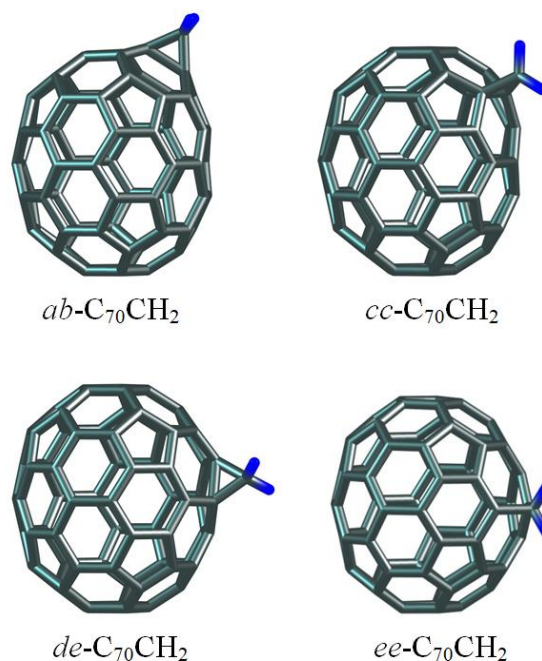


Fig. 5. Regioisomeric cyclopropano-derivatives of fullerene C_{70} .

Note the optimization of the initial geometries lead to the 6.6-closed structures except of ee - $C_{70}CH_2$, in which ee -bond becomes open. This result agrees with the previous theoretical and experimental study [35]. We considered ee -isomer with other 6.6-adducts of C_{70} , as its functionalization in all structures occurs *via* 6.6 bonds. Furthermore, ee - $C_{70}CH_2$ is thermodynamically most stable compound in the isomeric series [36]. The computed thermodynamic and information entropies of molecules $C_{70}CH_2$ are collected in Tables 3 and 4.

According to the computations, the thermodynamic and information entropies of the $C_{70}CH_2$ isomers are changed symbatically (Figure 6). The most (ee - $C_{70}CH_2$) and the least (de - $C_{70}CH_2$) symmetric isomers of $C_{70}CH_2$ demonstrate minimal and maximal h and S° values, respectively. Notably, ee - $C_{70}CH_2$, the most stable

compound in the set [36] is characterized with the lowest entropies.

Table 3. Thermodynamic entropy of the $C_{70}CH_2$ regioisomers ($J mol^{-1} K^{-1}$)

Regioisomer	Contributions to the total value			S°_{tot}
	S_{trans}	S_{rot}	S_{vib}	
<i>ab</i>	193.1	161.6	299.6	654.2
<i>cc</i>	193.1	161.5	298.1	652.7
<i>de</i>	193.1	161.5	303.1	657.6
<i>ee</i>	193.1	155.8	298.5	647.3

Table 4. Symmetry, partition and information entropy of the $C_{70}CH_2$ regioisomers

Regioisomer	Symmetry	σ	Partition over atom types	h (bit/atom)
<i>ab</i>	C_s	1	$5 \times 1 + 34 \times 2$	5.258
<i>cc</i>	C_s	1	$7 \times 1 + 33 \times 2$	5.286
<i>de</i>	C_1	1	73×1	6.190
<i>ee</i>	C_{2v}	2	$1 \times 1 + 36 \times 2$	5.204

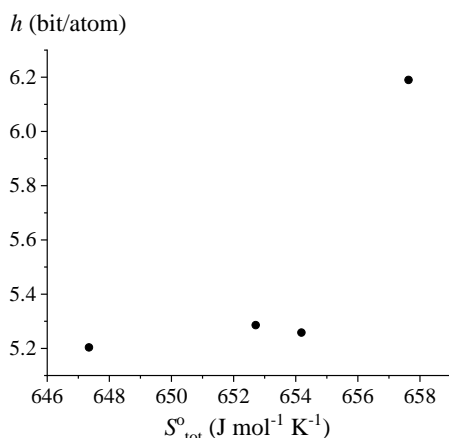


Fig. 6. Thermodynamic vs. information entropies of the 6.6-monoadducts $C_{70}CH_2$.

3.4 General remarks

At the end we compare the cases of all studied fullerene adducts with fullerenes themselves. In the case of the C_{60} isomers, the previously found ranges for information and thermodynamic entropies were 0...5.907 bit/atom and 548.5...591.3 $J mol^{-1} K^{-1}$ (the PBE/3 ζ calculations [15]). The symmetry varies in that work from I_h to C_1 . A slightly narrower range was found for h values of the C_{84} fullerene isomers, 1.950...6.392 bit/atom, whereby the symmetry point groups were between D_{6h} and C_1 [37]. Those ranges are much wider than the ranges found in this work for the fullerene adducts (cf. Tables 1–4). Symmetry point groups of the fullerene adducts vary between D_{2h} and C_1 , i.e. the symmetry of the fullerene derivatives possesses lower diversity. Thus, the isomerism of the fullerene skeleton has greater effect on

the entropy than the positional isomerism associated with the different location of the addends on the fullerene core.

4 Conclusions

We have obtained the quantitative estimates of the thermodynamic and information entropies of the cyclopropane derivatives of the C_{60} and C_{70} fullerenes with one and two addends. We did not find the correlations between these entropies and symmetry of the molecules. However, the h and S° values are changed symbatically with the increase/decrease of the symmetry point groups of molecules $C_{60/70}(CH_2)_{1-2}$. This regularity is recommended for digital selecting most and least symmetric structures in the series of isomeric fullerene adducts (e.g., lower and higher information entropies correspond to most and least symmetry structures). A digital classification within the correlation field is complicated because different partitions and, consequently, different information entropies may correspond to the same symmetry point group. However, we think that it is possible to work with h values within the correlation field with invoking additional structural descriptors [37].

Acknowledgment

Denis Sabirov is grateful to Prof. Jean-Claude Serge Levy (Université Paris Cité) for the discussion on the present work under 9^{èmes} Journées Complexité-Désordre (June 19–20, 2023, Paris, France).

Funding

This research was funded by the Russian Science Foundation, project “Information entropy of chemical reactions: A novel methodology for digital organic chemistry”, grant number 22-13-20095.

References

1. D.S. Sabirov, I.S. Shepelevich, Entropy **23**, 1240 (2004).
2. M. Rahul, J. Clement, Ain Shams Eng. J. **14**, 102542 (2023).
3. S. Govardhan, S. Roy, Eur. Phys. J. Plus **138**, 670 (2023).
4. D.A. Banaru, S.M. Aksenov, N.A. Yamnova, A.M. Banaru, Crystallogr. Rep. **68**, 223 (2023).
5. R. Guha, D. Velegol, J. Cheminf. **15**, 54 (2023).
6. T. Augustine, R. Santiago, Symmetry **15**, 635 (2023).
7. K. Jacob, J. Clement, M. Arockiaraj, D. Paul, K. Balasubramanian, J. Mol. Struct. **1277**, 134786 (2023).
8. D.S. Sabirov, O. Ori, A.A. Tukhbatullina, I.S. Shepelevich, C – J. Carbon Res. **8**, 24 (2022).
9. S.V. Krivovichev, V.G. Krivovichev, R.M. Hazen, S.M. Aksenov, M.S. Avdontceva, A.M. Banaru, L.A.

- Gorelova, R.M. Ismagilova, I.V. Korniyakov, I.V. Kuporev, S.M. Morrison, T.L. Panikorovskii, G.L. Starova, *Mineral. Mag.* **86**, 183 (2022).
10. S.C. Basak, B.D. Gute, G.D. Grunwald, *J. Chem. Inf. Comput. Sci.* **37**, 651 (1997).
11. S. Basak, D. Harriss, V. Magnuson, *J. Pharm. Sci.* **73**, 429 (1984).
12. D. Bonchev, D. Kamenski, V. Kamenska, *Bull. Math. Biol.* **38**, 119 (1976).
13. D. Bonchev, *Bulgar. Chem. Commun.* **28**, 567 (1995).
14. D.S. Sabirov, A.A. Tukhbatullina, I.S. Shepelevich, *Symmetry* **14**, 1800 (2022).
15. D.S. Sabirov, E. Osawa, *J. Chem. Inf. Model.* **55**, 1576 (2015).
16. D. Sabirov, *Comput. Theor. Chem.* **1123**, 169 (2018).
17. D.S. Sabirov, O. Ori, A.A. Tukhbatullina, I.S. Shepelevich, *Symmetry* **13**, 1899 (2021).
18. D.S. Sabirov, A.A. Tukhbatullina, *Nanomaterials* **12**, 4404 (2022).
19. D.S. Sabirov, V.I. Sokolov, O.A. Terentyev, *RSC Adv.* **6**, 72230 (2016).
20. A. Banaru, S. Aksenov, S. Krivovichev, *Symmetry* **13**, 1399 (2021).
21. S. Krivovichev, *Mineral. Mag.* **77**, 275 (2013).
22. M. Yamada, T. Akasaka, S. Nagase, *Chem. Rev.* **113**, 7209 (2013).
23. A.R. Tuktarov, A.R. Akhmetov, D.Sh. Sabirov, L.M. Khalilov, A.G. Ibragimov, U.M. Dzhemilev, *Russ. Chem. Bull.* **58**, 1724 (2009).
24. A.R. Tuktarov, V.V. Korolev, D.S. Sabirov, U.M. Dzhemilev, *Russ. J. Org. Chem.* **47**, 41 (2011).
25. T. Liu, I. Abrahams, T.J.S. Dennis, *J. Phys. Chem. A* **122**, 4138 (2018).
26. A.V. Mumyatov, P.A. Troshin, *Energies* **16**(4), 1924 (2023).
27. P.A. Troshin, H. Hoppe, J. Renz, M. Egginger, J.Y. Mayorova, A.E. Goryachev, A.S. Peregudov, R.N. Lyubovskaya, G. Gobsch, N.S. Sariciftci, V.F. Razumov, *Adv. Funct. Mater.* **19**, 779 (2009).
28. D. He, X. Du, Z. Xiao, L. Ding, *Org. Lett.* **16**(2), 612 (2014).
29. S. Sumino, F. Matsumoto, T. Iwai, T. Ito, *J. Org. Chem.* **86**(12), 8500 (2021).
30. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
31. D.N. Laikov, Y.A. Ustynyuk, *Russ. Chem. Bull.* **54**, 820 (2005).
32. Chemcraft, <http://www.chemcraftprog.com/> (accessed November 20, 2023)
33. *Standard Thermodynamic Properties of Chemical Substances* (CRC Press LLC, 2000).
34. C. Thilgen, A. Herrman, F. Diederich, *Angew. Chem. Int. Ed. Engl.* **36**, 2268 (1997).
35. K. Raghavachari, C.M. Rohlfing, *Chem. Phys. Lett.* **197**, 495 (1992).
36. B. Li, C. Shu, X. Lu, L. Dunsch, Z. Chen, T.J.S. Dennis, Z. Shi, L. Jiang, T. Wang, W. Xu, C. Wang, *Angew. Chem. Int. Ed. Engl.* **49**, 962 (2010).
37. D.S. Sabirov, O. Ori, I. László, *Fullerene Nanotube Carbon Nanostruct.* **26**, 100 (2018).